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ATMOSPHERIC TRANSPORT OF TOXAPHENE
TO LAKE MICHIGAN

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ABSTRACT

Atmospheric levels of toxaphene were monitored during the summer and fall of 1981 at 4 locations: Greenville, Mississippi, St. Louis, Missouri, Bridgman, Michigan, and Beaver Island, Michigan. Each collection was conducted by continuously sampling air during the first two weeks of the months of August, September, October, and November. The collected toxaphene was analyzed on a capillary equipped electron capture gas chromatograph. The average concentrations over the entire sampling period for each site were 7.39 ng/m³ in Greenville, 1.18 ng/m³ in St. Louis, and 0.27 ng/m³ for Lake Michigan (Bridgman and Beaver Island combined). The summer versus fall fluctuations in amount of toxaphene at each site was 0.44 ng/m³ versus 0.26 ng/m³ for Bridgman; 1.73 ng/m³ versus 0.63 ng/m³ for St. Louis; and 9.05 ng/m³ versus 4.34 ng/m³ for Greenville. The maximum monthly average occurred in September for all of these collections. Diagnostic modeling to describe possible air transport of toxaphene showed that at all receptor locations the air transport corridor for toxaphene was associated with southerly winds. The strength of this corridor increased from northern to southern measurement sites. A flux estimate for toxaphene deposition to the lake surface ranged from 3,360 to 6,720 kg/yr.

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INTRODUCTION

Occurrence of toxaphene in the Great Lakes ecosystem is possibly one of the most perplexing pollution problems to have ever occurred in this region. Detectable levels of toxaphene were first evident in fish collected in 1974 from Lake Michigan and reported by the U.S. Fish and Wildlife Service (Rappe et al. 1979). Subsequent to this, additional data have been reported which show toxaphene as a widespread contaminant of Great Lakes fish (Rice and Evans, in press). However, the use of toxaphene is primarily concentrated in the southern states with few known applications of this pesticide in the Great Lakes region. The sources of toxaphene input to the Great Lakes have not yet been determined. Difficulty in analyzing environmental samples for toxaphene has prevented thorough examination of the occurrence and distribution of toxaphene in the environment.

Like PCB, toxaphene is not just one compound. In fact, it is a mixture of at least 180 separate chemical compounds (Holmstead et al. 1974). This complex chemical makeup of toxaphene is the primary reason that its environmental fate is so poorly understood. Conventional packed column separation with electron capture detection is not adequate to precisely characterize toxaphene. Fortunately, capillary chromatography techniques have allowed better resolution of the component peaks and have improved the confidence with which toxaphene is identified in samples. However, selective weathering of the original toxaphene peaks is believed to greatly alter the ratio of peaks from the parent material (Zell and Ballschmiter 1980), as well as create new peaks which are derived from the parent toxaphene but cannot be used for matching and quantification in the usual sense. In a study of the

global distribution of toxaphene, Zell and Ballschmiter (1980) presented a technique using capillary separation and analysis of fish residues for chlorinated hydrocarbons which dealt with many of the analytical difficulties presented by toxaphene. In this method, fractionation of the extracts with florisil chromatography was carried out to reduce interferences from PCBs. This type of approach has also been successfully applied by others. Ribick et al. (1982) have analyzed fish tissues for toxaphene using silica gel fractionation and capillary chromatography while others have relied on silica or florisil separation and packed column analyses (Schmitt et al. 1981, Bidleman et al. 1978, Devault et al. 1982). All of these techniques are based on chromatographic methods which rely on retention time matching as the basis for identification. However, these techniques do not provide absolute chemical confirmation. To date, exact identification of only 11 of the 177 constituents in standard toxaphene has been made (Korte et al. 1979). Exact chemical identification of environmental residues, however, is difficult under the best conditions because levels are usually low and many inferences have to be made. Furthermore, toxaphene poses additional problems because standard electron impact mass spectrometry is relatively insensitive to the components of toxaphene. Positive chemical ionization techniques with mass spectrometry have been used to identify some toxaphene components in residues from fish from the Great Lakes (Ribick et al. 1982) and this is the only verification to date that absolutely confirms the presence of toxaphene in Great Lakes fish.

Because of the analytical difficulties in measuring toxaphene in environmental matrices, this study is as much an analytical methods study as it is a study of environmental distribution. As already mentioned, the perplexing question about toxaphene in the Great Lakes is "How is it getting there?"

The choices are limited as uses of this insecticide in the Great Lakes area are few, with the preponderant uses occurring in the cotton and soybean growing areas of the United States, e.g. the Cotton Belt. Some use has been reported for the Great Plains States, however for 1972 the total of 0.5 million lbs. used by all the states from the region was only 1% of the Cotton Belt usage. In 1980, South Dakota used about 0.14 million lbs. of toxaphene which would represent about 1% of estimated 1980 U.S. usage (Rice and Evans, in press). No evidence for accidental spillage has been uncovered, and manufacturing is not located in any of the Great Lakes states. One proposal contended that pulp bleaching may inadvertently produce toxaphene-like materials in its waste liquor. However, controlled laboratory tests under optimal conditions for chlorine substitutions of pulping waste liquors could not produce toxaphene-like compounds with greater than three chlorine atoms (presented by David Stalling, U.S. Fish and Wildlife Service, at EPA hearing for cancellation of toxaphene, July 1982); toxaphene is composed mainly of six to nine chlorine-containing compounds. To many scientists, the only logical choice left seems to be atmospheric transport. Direct observations of this, however, are limited.

There is a good deal of experimental evidence to suggest that chemicals like toxaphene, PCB, and DDT can be transported via the air for thousands of miles (Bidleman and Olney 1974, Seba and Prospero 1971, Risebrough et al. 1968). These data are strengthened by results from radioactive fallout studies and by the recent concern over acid rain and its atmospheric link to industrial centers.

There are literature data to support the contention that high amounts of toxaphene can be lost due to volatility (Nash et al. 1977, Sieber et al.

1979). Long-range transport of toxaphene by way of the air is well documented both by direct observation of toxaphene in air at remote sites (Bidleman and Olney 1975, Bidleman et al. 1981) and by inference from finding the material in organisms at sites remote from the use of this material: Great Lakes fish (Rappe et al. 1979); Antarctic cod from the South Pacific and an Arctic char from the Tyrolean Alps (Zell and Ballschmiter 1980); and an Arctic char from a lake in southern Sweden (Jansson et al. 1979).

Use of air mass trajectory analyses coupled with pollutant measurements is a relatively new procedure for confirming sources of these materials. Pack et al. (1977) used a trajectory model to map fluorocarbon transport in Europe. Others have performed long range mapping to follow ozone transport along the eastern coastline (Wolff et al. 1977). Trajectory modeling was used by Rice and Olney (1978) to confirm that toxaphene transport to Bermuda could be tied to the southeastern region of the U.S. This same type of trajectory modeling was utilized in this study in order to determine if a transport link to the cotton-growing regions (South Central to Southeast U.S.) could be established which coincided with high episodes of toxaphene occurring over Lake Michigan.

Measurements of toxaphene in air, rain and surface water of the Great Lakes have been reported (Rice and Evans, in press). Therefore, the potential for this route appears possible. The purpose of this study was to examine atmospheric transport of toxaphene to the Great Lakes from the high-use areas in the southern United States. Establishing a reliable analytical method became one of the most critical requirements to achieving this goal.

METHODS

AIR COLLECTION

Toxaphene in the air was collected by passing air through an air scrubbing system composed of a glass fiber filter [only with the Hi-Vol® (General Metals Works, Inc., Village of Cleves, Ohio) collectors], and a series of soft polyurethane foam plugs. Two types of collectors were used in this study. A Hi-Vol® collector was used for sampling air for toxaphene where concentrations were anticipated to be low to moderate, e.g. at the Lake Michigan sampling locations on Beaver Island and at Bridgman, Michigan, and in St. Louis, Missouri. A low volume air sampling device was used in Greenville, Mississippi, where levels were anticipated to be high. The high volume sampler was a standard Hi-Vol® high volume sampling system modified by adding a stainless steel extension tube (23 cm long and 9 cm dia.) behind the filter holder (10 x 8") such that two to three 9-cm diameter x 6.5 cm long polyurethane foam plugs could be installed. The air first passes through a Gelman type "A" glass fiber filter rated at an exclusion size for aerosols in air of 1 μ m. The bulk of the toxaphene is expected to be collected as a gas on the first foam plug. The second plug in the series was placed as a backup to check for possible breakthrough of toxaphene and to also preclude back flow of contamination from the pumping apparatus. The pump was a General Metal Works model GMWL-2000 blower.

The entire sample holder was carefully cleaned prior to use by scrubbing with soap and water, and solvent rinsing with pesticide grade acetone and methylene chloride. Between each sample collection the collection assembly was additionally rinsed with pesticide grade solvents. The filter and plugs were carefully cleaned prior to use to free them of possible contaminants.

The procedure for cleaning filters involved 450°C ignition in a muffle furnace for 4 hours and storage in individual aluminum foil containers. The plugs were carefully cleaned prior to use according to the procedures of Billings and Bidleman (1980), and periodically checked to guarantee their cleanliness prior to use.

Polyurethane foam plugs were also used for low volume collection. These plugs measured 7 cm long x 3.5 cm diameter and were installed in glass holders (10.5 cm long x 3.5 cm diameter). No prefilters were used with these collectors and two plugs were placed in series. These plugs were also precleaned according to Billings and Bidleman (1980).

The flow for the Hi-Vol® collection was maintained at 0.55 to 1.1 m³/min and the volumes for collection ranged from 1,161 to 4,100 m³ (Table 1). The flow for the low-volume collection ranged from 7 to 10 L/min for the short day collections and 2 to 5 L/min for the monthly average collections. A Gast pump was used to provide the vacuum for the low-volume collector and a Gilmont flow meter (size #3, Cat. #F1300) was used to monitor the flow by taking readings at 1 to 2-day intervals throughout the collection. A Sprague/Textron Gas Meter was used to measure the monthly air volumes collected. These units were calibrated at the University of Michigan Air Resources Laboratory prior to employment. To monitor the airflow of the Hi-Vol® collections, a Marshalltown type flow gauge was used at Bridgman and Beaver Island. Use of these gauges involved observation of the gauge reading 2 to 3 times during the 3-day sampling period and deriving an average reading for the total period of collection. With the St. Louis collection, a continuous disc chart recorder monitored the gas flow. All of the General Metal Works pumps and gauges for

TABLE 1: AMOUNT OF TOXAPHENE IN AIR SAMPLES FROM BRIDGMAN, MICHIGAN;
BEAVER ISLAND, MICHIGAN; ST. LOUIS MISSOURI; AND GREENVILLE, MISSISSIPPI

SAMPLE LOCATION	DATE-TIME ON	DATE-TIME OFF	AIR VOLUME (M ³)	PEAK MATCHING (# USED / # POSS.)	TOXAPHENE CONC. (NG/M ³)
BRIDGMAN, MICH.	07/30-1755	08/02-1605	3456	09/34	.32
	08/02-1615	08/05-1515	3353	11/39	.04
	08/05-1525	08/08-1550	3506	16/34	.02
	08/08-1600	08/11-1620	3146	06/34*	.69
	08/25-1620	08/28-1230	3211	13/34*	1.17
	08/28-1240	09/03-1130	6727	22/34	.63
	09/03-1115	09/06-1635	4074	07/39*	.16
	09/28-1732	09/30-1714	2148	17/39	.09
	10/01-1808	10/04-1210	3960	08/34	.01
	10/09-1630	10/11-1609	2916	14/41*	.67
	10/14-1853	10/17-1645	4192	10/41*	.46
	11/05-1806	11/08-1213	4364	10/41*	.17
	11/08-1236	11/12-1236	4729	12/32	.08
	11/14-1742	11/17-1745	3549	18/26	.50
	08/28-1530	08/31-1600	3924	19/39	.05
	08/28-1530	08/31-1600	3985	18/34	.02
BEAVER IS., MICH.	08/31-1630	09/03-1630	4709	09/32*	.23
	08/31-1630	09/03-1630	3586	10/26	.28
	09/28-1715	10/01-1530	4131	14/34	.02
	09/28-1715	10/01-1530	4538	10/32*	.03
	10/01-1600	10/04-1630	3871	11/39	.03
ST. LOUIS, MO.	07/30-1530	08/02-1530	4100	19/60*	.47
	08/02-1530	08/05-1530	3577	17/60*	.56

TABLE 1. (continued)

SAMPLE LOCATION	DATE-TIME ON	DATE-TIME OFF	AIR VOLUME (M ³)	PEAK MATCHING (# USED / # POSS.)	TOXAPHENE CONC. (NG/M ³)
	08/05-1530	08/08-1530	2540	14/34	4.69
	08/08-1530	08/11-1530	3058	09/60*	.51
	08/25-1200	08/28-1200	3326	32/60*	5.24
	08/28-1200	08/31-1200	3192	18/42*	.86
	08/31-1200	09/03-1200	2661	16/42*	.97
	09/03-1200	09/06-1200	2925	14/42*	1.16
	09/28-1530	10/01-1530	3452	09/26	1.00
	10/01-1530	10/04-1530	3542	14/26	.40
	10/04-1530	10/07-1530	3758	09/26	.75
	10/07-1530	10/08-1345	1161	12/26	.51
	11/05-1530	11/08-1530	3884	15/26	.52
	11/08-1530	11/11-1530	3456	09/26	.37
	11/11-1530	11/12-2100	1680	09/26	1.03
GREENVILLE, MISS.	07/30-1630	08/02-1630	38.23	14/68	4.28
	08/02-1630	08/05-1630	42.55	49/68	8.07
	08/05-1630	08/08-1800	43.44	34/68	10.71
	08/08-1800	08/11-1800	39.74	26/68	2.79
	08/25-0430	08/28-0900	39.93	33/68	7.90
	08/28-1830	08/31-1800	37.32	34/68	7.76
	07/30-1630	08/28-0915	99.71**	35/40	4.43
	09/03-0630	09/06-1800	43.09	26/40	17.79
	09/01-2100	09/28-2100	185.47**	33/68	1.89
	09/28-2100	10/04-2100	69.55	32/68	3.70
	10/04-2100	10/07-2100	34.78	27/40	7.37
	10/07-2100	10/10-2100	37.37	29/68	5.68
	10/10-1100	10/13-1100	10.20	23/40	22.44
	11/02-1000	11/05-1000	32.40	24/40	4.89

(continued)

TABLE 1. (continued)

SAMPLE LOCATION	DATE-TIME ON	DATE-TIME OFF	AIR VOLUME (M ³)	PEAK MATCHING (# USED / # POSS.)	TOXAPHENE CONC. (NG/M ³)
	11/05-1000	11/11-1000	64.80	17/40	3.07
	11/11-1000	11/14-1000	32.40	14/40	2.62
	11/14-1000	11/17-1000	32.40	13/40	1.79
	10/22-1000	11/19-1000	201.60**	24/40	.99

* The relative retention time standard was p,p'-DDE for these samples; otherwise, octochloronaphthalene was used.

** Long duration samples.

the Hi-Vol® samples also were calibrated on the University of Michigan Air Resources Laboratory gas meter prior to use in the field.

The air collectors were operated at locations which were selected to describe a possible transport pathway for toxaphene from Greenville, Mississippi, a region known for high use of toxaphene in the past, to Lake Michigan. Three locations, Greenville, Mississippi, St. Louis, Missouri, and Bridgman, Michigan (Figure 1) were sampled simultaneously during four 2-week time intervals through the summer and fall of 1981. Samples were also collected from Beaver Island, in northeastern Lake Michigan, during the second and third collection period. Rain was collected from Beaver Island during the last sampling interval and also in April before air collection began in the spring. Several attempts were made to collect rain at Bridgman. However, the sample collectors were vandalized in each instance and no rain samples were obtained. The rain collectors were simple bucket collectors (total fallout collectors) which were outfitted with screen wire rings on the top edges to discourage birds from landing on them. The buckets were carefully washed with soap and water and rinsed with pesticide grade methylene chloride just prior to each use. For storage, the contents of the buckets were poured into pre-cleaned brown glass 1-gal bottles. The interior of the buckets were rinsed with methylene chloride and these rinses were added to the sample bottles. Additional methylene chloride (total 200 mL/bottle) was added for stabilization in storage.

Periodic blanks were taken at each of the sampling locations. These involved all the steps of the setup for collection except for turning on the pumps. These samples were then broken down and returned to the laboratory for extraction and analysis as if they were actual samples.

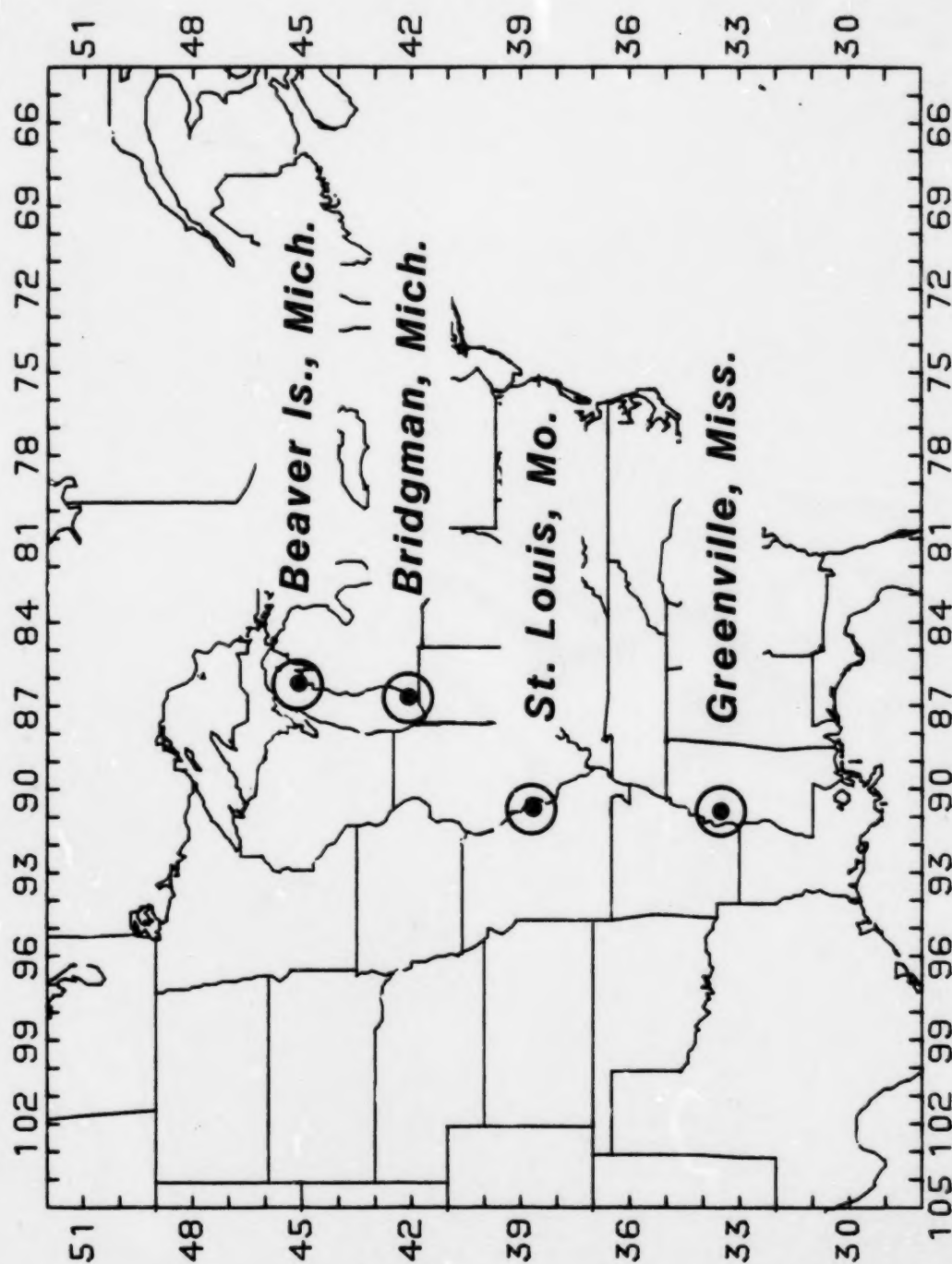


Figure 1. Locations of the four sites where air was sampled for toxaphene in the summer and fall of 1981.

EXTRACTION

To extract the toxaphene residues from the filters and foam plugs, each was cycled with pesticide grade petroleum ether for 12 hr in a Soxhlet assembly. Following petroleum ether extraction, extracts were concentrated to approximately 5 to 10 mL and stored until analysis. The rain samples were extracted by mixing the sample with methylene chloride (1:3 v:v solvent to water) on a ball-mill roller for 3 hrs. Much thought went into how to work up the samples in a way that would maximize the identification of the toxaphene expected in the sample. Our major interests were to study any weathering which might be apparent and to avoid lengthy handling procedures which might reduce our recoveries. Nitration as a cleanup (Klein and Link 1970) was considered but discarded because some chemical alteration by the procedure had been reported (Ribick et al. 1982). Silicic acid (Bidleman et al. 1978) was repeatedly tested, however reproducibility was variable and we felt the results couldn't be trusted. Some of these tests are reported in Appendix A. We finally settled on a simple treatment of the extracts with sulfuric acid, followed by direct injection and analysis by electron capture gas chromatography.

CHROMATOGRAPHIC ANALYSIS

Analyses of the extracts involved concentration of each sample to 1 to 2 mL, acid treatment with an equal volume of concentrated sulfuric acid, transfer of the organic phase, and then an initial prescreening of each sample by packed column electron capture gas chromatography. Based on these initial prescreenings, the volume was adjusted for final qualitative and quantitative analyses by the capillary GC. For most of these final capillary injections,

a Varian 8000 auto-sampler was used. The injection volume was 4 μ L and the solvent was petroleum ether or hexane. The injection method was splitless with a back flush delay of 0.75 minutes. A toxaphene standard was usually injected for each of four samples injected. The operating conditions for the capillary instrument were as follows: the column was a (0.20 mm I.D. by 50 m long) Hewlett Packard fused silica capillary column coated with SE-54, the carrier gas was hydrogen flowing at a linear velocity of 35 cm/min, and nitrogen was used as the makeup gas flowing at 30 mL/min. The temperature program was 100° to 240°C at the rate of 1°C/min, and the other heated zones were 220°C injector and 320°C detector. Data handling for the capillary instrument was carried out using a Perkin-Elmer Sigma 10 data system with a basic programming upgrade. To ensure proper data slicing, i.e., discrete area slicing in small enough intervals to collect the capillary output, the Perkin Elmer standard slicing option was overridden by forcing the instrument to operate at its maximum slicing time of 0.13 sec/scan at 10 minute intervals. This was determined by trial and error to give the best data treatment to the entire spectrum of each 140-minute sample run. The method for processing the data was set to quantitate according to the external standard method. The retention times were calculated as relative retention times (RRT) to octachloronaphthalene which was used as the reference peak. DDE was used as a reference peak for some of the samples (refer to Table 1). These standards were added to each sample just prior to GC analyses. Relative retention time of the reference peak was set to 10 so as to get an additional decimal place listing from the relative retention time output of the Perkin Elmer data system (i.e., the Sigma 10 only prints three figures after the decimal), and achieve greater precision for peak matching.

To select a standard which most consistently matched the peaks that were being measured in the Greenville air samples, we examined three different toxaphene formulations used in the Greenville area (Hercules BFC 90-100, Central American 90-100, and Drexel 616 Form Chem). These were compared to our EPA Research Triangle Park standard (Lot #B610). From this study we decided that the EPA standard gave the best matches (Appendix B).

In order to establish an appropriate representation of toxaphene to be used for comparison with samples, standards were screened and peaks were chosen based on the following criteria. Only peaks that were well resolved and could be reproducibly identified between standard runs were considered. In order to achieve reproducibility in peak identification, i.e., RRT matching, while minimizing the inclusion of close eluting peaks within the peak window, an RRT tolerance of ± 0.008 was chosen. Furthermore, it was considered important that an even distribution of peaks over the total elution time for toxaphene be used. Approximately 90 peaks were selected based on the above criteria. The selected peaks were then screened against expected interferences. For this study Aroclors 1242 and 1254 were especially important in the Lake Michigan and St. Louis samples, and the pesticides DDT, DDE, and chlordane were important interferences in Greenville. Those peaks which were matched with the various interfering components were removed from the peak table. During the course of our analyses, the number of peaks which met all screening criteria for standards ranged from 26 to 60 (c.f. Table 1). These peaks were then used to represent toxaphene for comparison with samples.

Toxaphene identification in the samples was accomplished by screening sample peaks for matches with the standard peak tables described above. The criteria for peak matching in the samples was identical to those used for

standard comparison. However, those peaks that were matched in the samples were further screened for possible errors in baseline treatment, and unknown interferences. Peaks occurring in the sample that were disproportionately high in area (relative to other matched peaks) were considered interfered with and were excluded from quantitation. This latter screening presupposes that the ratio of toxaphene peaks in the sample is similar to the standard. Lacking proof of this, we selectively eliminated peaks only in the most extreme case, e.g., when the (interfered) peaks accounted for greater than approximately 40 percent of the sum of the area for all of the matched peaks.

Quantitation of toxaphene in the samples was based on the ratio of the sum of the areas for peaks matched (and screened) in the sample to the sum of the areas of the corresponding peaks in the standard. This value was then multiplied by the standard concentration and sample volume to determine the total ng of toxaphene. The toxaphene concentration was the quotient of total nanogram of toxaphene determined to be in the sample divided by the volume of air (m^3) collected (Table 1). Representative chromatograms of samples and standards containing toxaphene are shown in Figure 2.

QUALITY ASSURANCE

Blanks were found to contain no recognizable toxaphene patterns. However, some spurious peaks did match the relative retention times for toxaphene and upon quantitation averaged 23.1 ng. Therefore, the limit of detection for the high volume samples was $0.06 \text{ ng}/\text{m}^3$ and for the low volume samples it was $0.6 \text{ ng}/\text{m}^3$. Linearity checks for electron capture response to toxaphene were performed over the standard ranges of 118 to 444 ppb and, generally, linearity was good for the total mass of peaks (Figure 3).

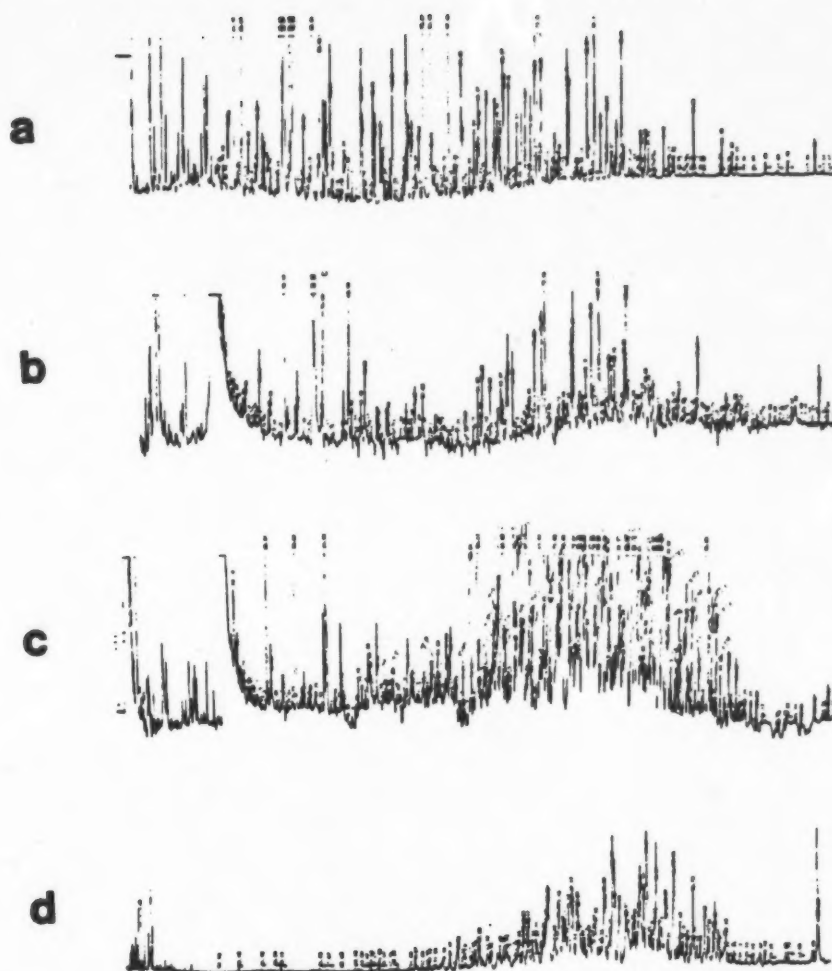


Figure 2. Capillary chromatograms of toxaphene-containing air, rain and fish samples and EPA toxaphene standard. The sculpin sample was analyzed on another project and is provided for comparison of the atmospheric data with biological residues. a) Air sample from Beaver Island (28 August to 31 August 1981) containing 0.054 ng/m^3 toxaphene; b) Rain sample from Beaver Island (28 September to 2 October 1981) containing 31.58 ng/L toxaphene; c) Sculpin composite sample from Lake Michigan (17 June 1982) containing 0.718 ng/gm toxaphene; d) toxaphene standard ($4 \text{ } \mu\text{L}$ of 118 ng/mL). G/C conditions -50 m fused silica column coated with SE-54 and temperature-programmed from 100 to 240°C at $1^\circ/\text{min}$.

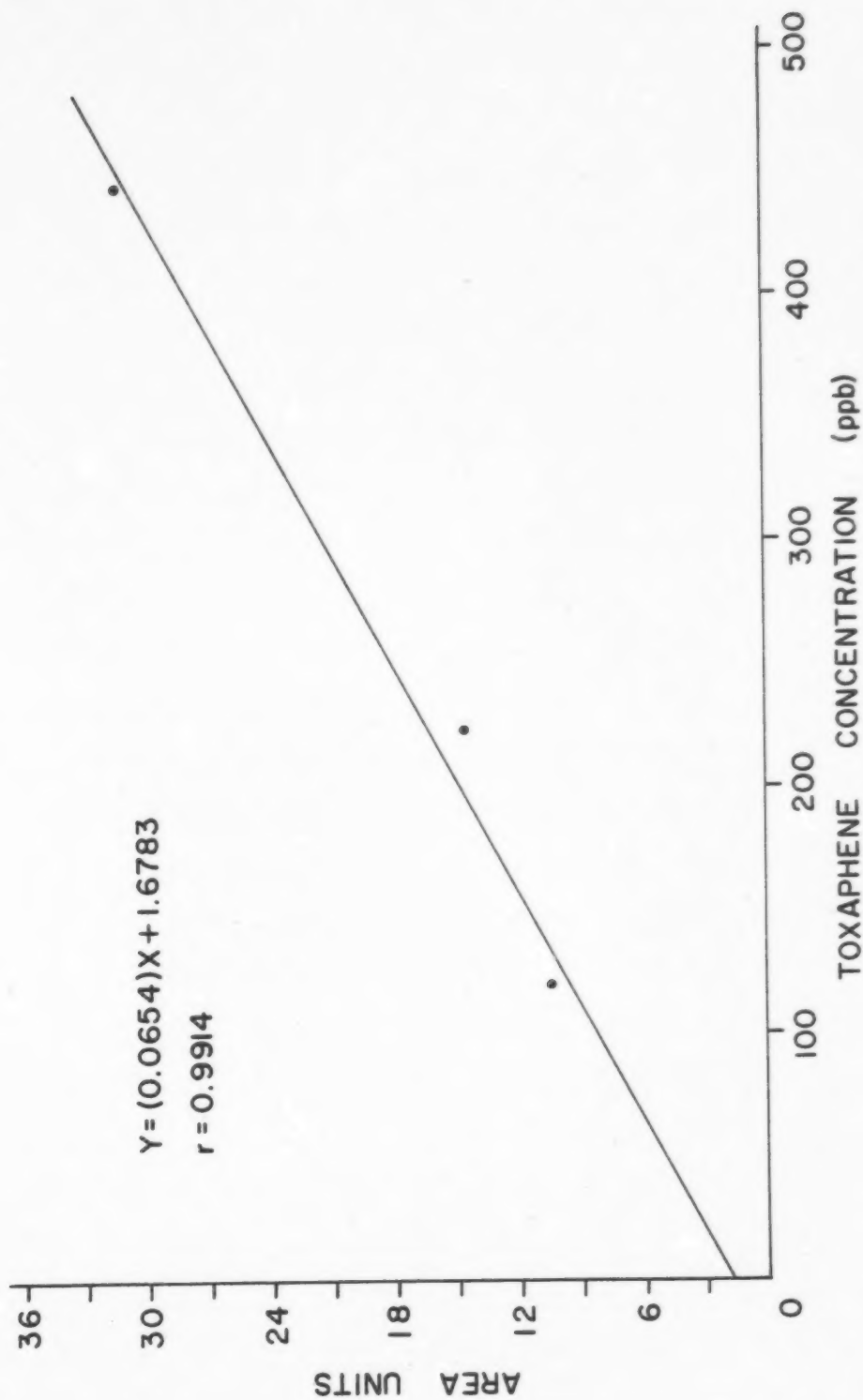


Figure 3. Linearity plot of the electron capture detector response to toxaphene. Plotted are the observed areas for the toxaphene standards versus their concentration (118, 222, and 444 ppb).

Consistent linearity was not observed for the individual peaks, however. This may bias our results as different assortments of selected peaks are used. A thorough test for this was beyond the scope of this study. However, we observed the following: In general, the ECD response of smaller, earlier eluting peaks tended to exhibit greater linearity within the range of concentrations tested than did larger, later eluting peaks. In addition, the intercepts of the linearity plots for the smaller peaks tended to be negative while the intercepts for the larger peaks were generally positive. One conclusion from this treatment was that using a good spread of peaks over the range of those possible would cancel out this opposing linearity, therefore our peak selection procedure should have minimized this problem.

Duplicates were run at Beaver Island and reasonable replicate performance was observed, see Table 2.

TABLE 2. DUPLICATE RESULTS

Beaver Island Sample Date	Toxaphene Concentration (ng/m ³)		Relative % Difference of Duplicates
8/28	0.054	0.023	43
8/31	0.2335	0.2773	8
9/28	0.0237	0.0309	13
			$\bar{x} = 21$

Averaging the results for the three duplicate sets gave a value of 21 for the average relative percent differences of three duplicates.

A performance test was conducted using standard solutions of toxaphene and Aroclor 1254 provided by the Grosse Ile EPA laboratory in January of 1982.

MODELING

The atmospheric deposition of toxaphene into the Great Lakes is speculated to be the result of transport from regions far removed from the area. To assess this claim, diagnostic modeling tools have been developed and applied to the measured values of toxaphene for three of the sampling sites. The diagnostic techniques used in this study take into account the potential long-range transport of toxaphene and can include enroute processes of dry and wet deposition, chemical transformation, and dispersion. The areal probability of contribution to the toxaphene levels at a receptor is calculated in two ways. In the first, the areal probability field resulting from the ensemble of individual trajectories arriving at the receptor during the hours of sampling is calculated. This is the probability of contribution due to "natural" phenomena. It would represent the spatial distribution of contribution if emissions were universally homogeneous. In the second method, the individual trajectory probabilities are weighted proportionally to the resulting toxaphene concentrations. If there is systematic transport of the toxaphene to the receptor from a particular area or areas, the two fields will be dissimilar. On the other hand, if there is no clear "corridor" associated with the transport of toxaphene, then there will be little difference between the weighted and unweighted contribution probability fields.

The assessment of potential long-range transport of atmospheric contaminants requires an estimation of the trajectory of the air prior to being sampled. In this study, the model of Heffter (1980) was used to calculate the upwind trajectories. The model estimates the height of the transporting layer by scanning temperature data from rawinsonde ascents, looking for stable layers 300 m or more above the surface. The bottom of the

transport layer is defined as the top of the layer of surface-induced wind shear. Typical transport depths in the Midwest United States are about 1,600 m during the summer months. Once the trajectory to the receptor has been estimated, the dispersion of material along the route is estimated based on the wind shear through the mixed-layer. Estimates of the rate of dispersion have been reported by Samson (1980), Samson and Moody (1980), and Draxler and Taylor (1982). In this work it is assumed that the dispersion of the contribution probability is linearly proportional to time. The area which could have contributed to the concentration at the receptor is determined through the integration of normally-distributed, two-dimensional "puffs" growing upwind of the receptor. Deposition of the contaminant en route to the receptor will reduce the potential for far upwind sources to contribute to the sample. The reduction, probably due to dry deposition, has been expressed by use of a dry deposition velocity, V_d . The diagnostic techniques used in this study allow the dry deposition velocity to be varied both diurnally and seasonally to account for varying atmospheric stability and surface conditions. Slinn (1982) has estimated that if the surface is a perfect sink for the pollutant, the deposition of the pollutant can be estimated by estimating the rate of transport of the pollutant to the surface via atmospheric mixing. Without better estimates of the dry deposition rates for toxaphene, such estimates are no more justifiable than assuming no deposition en route. In this study the dry deposition of toxaphene has been ignored for lack of reliable estimates of its rate of uptake at the surface. This assumption has no impact upon the results of this study because we are studying the relative difference in potential between two fields computed using the same assumptions. Similarly, the wet removal of toxaphene en route

to the measurement locations would affect the potential of upwind source regions to contribute, but little is known about wet deposition of the toxaphene. Differential distributions of precipitation could have an impact upon even the relative difference in probability, but quantitative estimates of precipitation rates for 1981 are not yet available from the National Climatic Center. While this limits the interpretation of results, the comparison of weighted versus unweighted contribution fields still provides a useful first test of the hypothesis that the toxaphene is being transported to the receptors from source fields in the southern United States.

RESULTS AND DISCUSSION

The concentrations of toxaphene measured in the air collected at the four sampling sites are listed in Table 1. The levels were highest in Greenville, Mississippi (average of 7.39 ng/m^3 - monthly collections not included), followed by St. Louis, Missouri (1.18 ng/m^3), and lowest in Bridgman (0.35 ng/m^3), and Beaver Island, Michigan (0.09 ng/m^3). The listing for peak matching in Table 1 provides an estimate of the similarity of the material measured to the standard. These can also be calculated as percentage matches which allows direct comparisons to be made between locations. The mean percent matches for each of the sampled regions merging Beaver Island and Bridgman for the Lake Michigan segment were as follows: 36% for Lake Michigan, 38% for St. Louis, and 51% for Greenville. One interpretation of this might be that the toxaphene in Greenville is closer to the source than the material measured in air at St. Louis or near Lake Michigan. And that distance from the source causes changes in the composition of the toxaphene mixture (often expressed as "weathering"). Another interpretation might be

that the lower match percents are merely a function of the smaller amount of material in the samples at the more northern sites. Regression analyses on the amount of toxaphene measured versus the percentage of peak matched with each sample subset (Greenville, Bridgman, St. Louis, and Beaver Island), however, were not found to be significant. Therefore, the degree of alteration of the toxaphene mixture does, in fact, appear to be related to the distance from the likeliest source regions which we propose are in the Southern United States.

Table 1 also lists the total volume of air collected for each sample. Regression analyses of this parameter versus the concentration measured were carried out for each sample subset. No significant correlations were found for any of the high volume collections taken in the northern sampling sites. However a positive correlation was found for the Greenville site, i.e., the greater the air volume sampled, the lower the total nanogram amount. Even when the monthly collections, which tended to underestimate the real concentrations, were left out of the calculations, the correlations were still significant. This finding led to further tests to see if breakthrough of the toxaphene could be observed on the low volume backup plugs. Recall that the Greenville sampling plugs were smaller than the Hi-Vol® plugs. No toxaphene, however, was found on the backup plugs, therefore breakthrough did not appear to be occurring. This was consistent with extensive tests of polyurethane foam collection efficiency for trapping of toxaphene vapors (Rice et al. 1977, Billings and Bidleman 1980).

Since breakthrough was not occurring with the low-volume collectors, there appears to be no obvious explanation for the low values found for the monthly collections in Greenville. Possibly, with these high volumes (90 to

200 m³ of air) and the relatively high levels of toxaphene being collected, re-release of toxaphene from the collection plugs was occurring. Other factors which were also different for the monthly low-volume collection were the lower air flow used, i.e., 2 to 4 L/min vs. 5 to 10 L/min for the short duration low-vols, and also the length of time the samples were left out, 20 to 30 days versus 2 to 3 days. Any one or all of these factors may have contributed to the difference in results between the monthly collections and the shorter interval Greenville collections. Tests for collection efficiency of toxaphene under low-volume/long duration sampling conditions would be recommended if further work using this method is planned. Comparison of the low-volume collector (short duration) with simultaneous high-volume collections were performed in a previous study (C. P. Rice and C. E. Olney, unpublished results), and the two systems compared favorably. Therefore, we do not feel there is any problem in the short duration results.

Filter retention of toxaphene appeared to be less than 5% of the total measured toxaphene for the Hi-Vol[®] collections. A qualification is needed here, however, in that the error range for these measurements were relatively high. The peak matching percentage for most of the toxaphene identifications on the filters were 15% or less, i.e. 4 to 5 peaks of the 26 to 40 possible. Because of the low values for the filters and the high uncertainty connected with these results, only the first plug analyses were used in reporting the toxaphene amounts measured.

Figures 4 and 5 present the results listed in Table 1 in graphical form. It is apparent that for each of the locations an increase occurred in amount of toxaphene from the first sample period in early August to early September, whereupon a gradual decline in concentration was observed for the October and

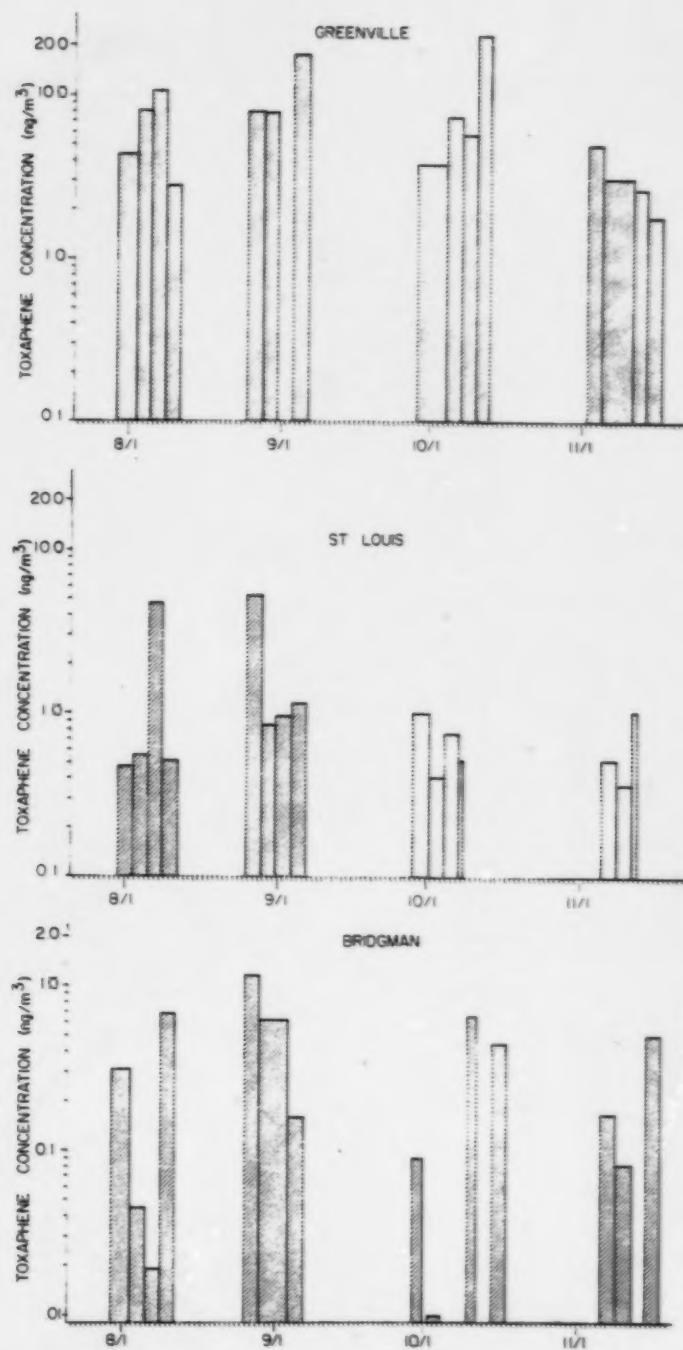


Figure 4. Simultaneous determinations of toxaphene in air measured at four sites lying along a general south-to-north transect from Greenville, Mississippi, through St. Louis, Missouri, and ending in the Lake Michigan area (Bridgman and Beaver Island, Michigan). The vertical axes are in log units and the horizontal axes are calendar dates.

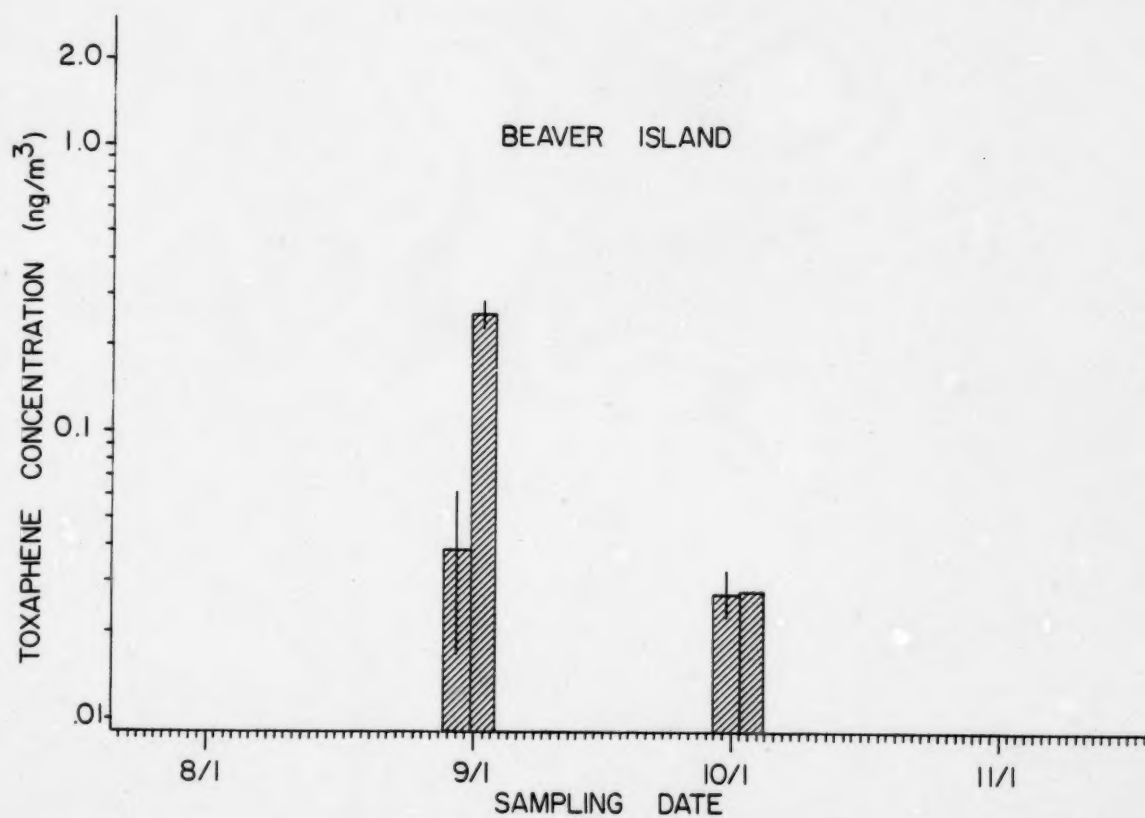


Figure 5. Toxaphene in air measured at Beaver Island, Michigan, from 28 August to 4 October 1981. Vertical axis is in log units and the horizontal axis is in calendar dates.

November sampling periods. Table 3 presents these findings in average concentrations for each of these discrete sampling periods.

This trend for toxaphene levels in air observed in our data was similar to the trend for relative levels of atmospheric/toxaphene observed by Arthur et al. (1976) in the Mississippi Delta in 1972-1974. In Arthur et al.'s study, the maximum average toxaphene occurred in August/ September periods: 1,540 ng/m³ - Aug. '72; 269 ng/m³ - Sept. '73; 903 ng/m³ - Aug. '74. These average concentrations were considerably higher than measured by us. However, toxaphene usage is reported to be much less now than in the early 1970s (Larry Lane, Mississippi State University, Agricultural Experiment Station, Personal Comm.).

TABLE 3. TREND IN TOXAPHENE CONCENTRATION AT SAMPLING SITES FOR THE SUMMER AND FALL OF 1981

Sampling Interval	Average toxaphene concentration by location (ng/m ³)			
	Beaver Island, Michigan	Bridgman, Michigan	St. Louis, Missouri	Greenville, Mississippi
August		0.26	1.31	6.61
September	0.15	0.62	2.16	11.40
October	0.03	0.30	0.69	6.04
November		0.23	0.56	2.64

In looking at Figure 3, one might expect some similarities in concentration patterns between the three locations, especially if an atmospheric link is predicted. For example, the first interval bears a close resemblance in general pattern between St. Louis and Greenville. There appears to be a tendency to observe possible shifts by one sampling period of a high level of toxaphene observed at one location to an appearance of this material as a high level in a

more northerly location a few days later (notice such a connection for St. Louis to Bridgman for the first sampling period, Figure 4). Keep in mind that the scale for the Bridgman figure is a factor of ten less than the two other sites depicted.

One rain sample was collected from Beaver Island, Michigan, while air measurements were being made from 28 September to 2 October 1981. The sample contained 31.6 ng/L of toxaphene with 14 peaks matched out of 37 possible in the peak table. Another rain sample collected on 1 April 1981, also from Beaver Island, was found to contain 70.2 ng/L with 5 out of 37 peaks matched.

MODELING OF ATMOSPHERIC TRANSPORT

One goal of this study was to use these data as a basis for proposing some boundary limits for toxaphene transport and deposition to Lake Michigan. We chose an atmospheric transport model to assist in these estimates.

The "natural potential" for contribution to toxaphene concentrations at the Bridgman, Michigan, site is shown in Figure 6. This figure shows the probability of contribution in units of 10^{-8} km^{-2} . It is the area which would contribute to the concentration of toxaphene if emissions were homogeneous and constant over the grid. The plot shows that the highest occurrence of winds during the sampling periods was from the southwest of the receptor. Figure 7 shows the result of weighting each trajectory by the concentration measured at the time of arrival. It is assumed that each trajectory arriving through the sample period contributed equally to the sample loading of toxaphene. The results indicate that the basic structure of the contribution field is not substantially varied from the spatial pattern found for the unweighted case in Figure 6. The similarity of the two fields can be discerned only by

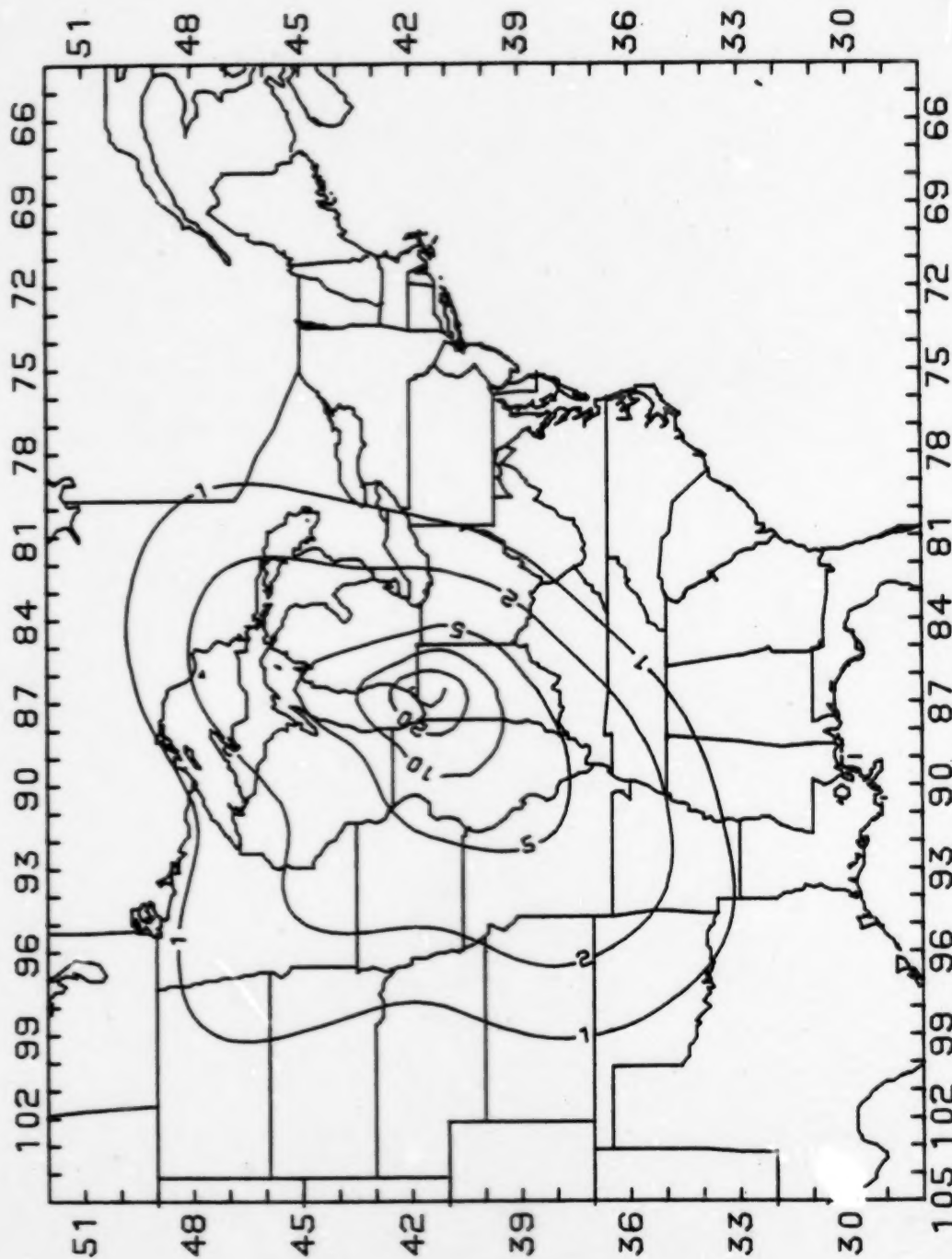


Figure 6. Unweighted probability of contribution during the sampling periods in units of $10^{-8}/\text{km}^2$ in Bridgman, MI. (approximate center of concentric rings).

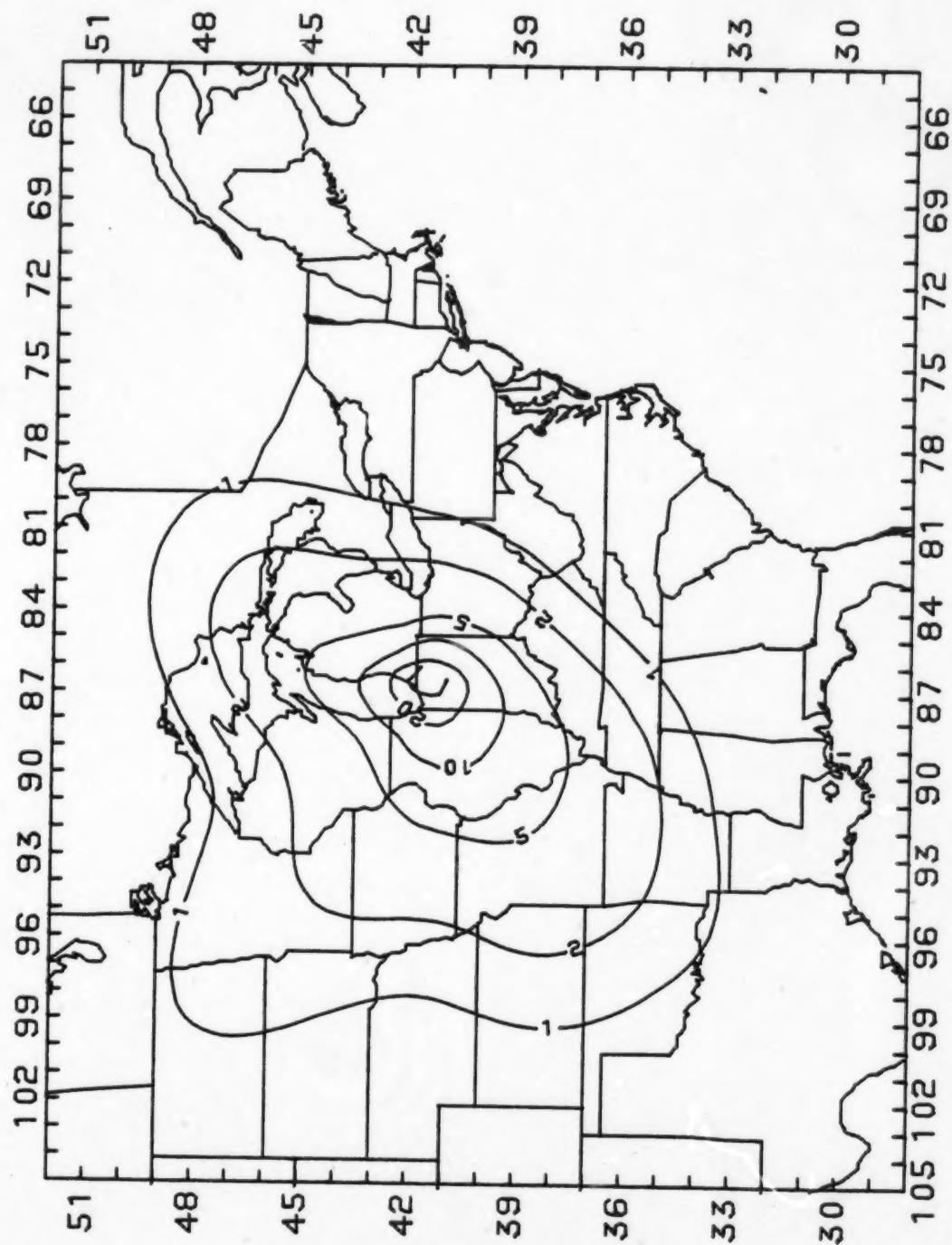


Figure 7. Weighted probability of contribution during the sampling periods in units of $10^{-8}/\text{km}^2$ in Bridgman, MI.

calculating the difference between the weighted and unweighted fields as shown in Figure 8. This plot suggests that there is a slight spatial bias (or corridor) for toxaphene, with higher concentrations associated with winds from the south to southeast, but the magnitude of the difference in the weighted and unweighted fields is small, being an order of magnitude lower than the magnitude of the probability of contribution field (Fig. 6).

Figures 9 and 10 show the unweighted and weighted fields, respectively, for the receptor at St. Louis, Missouri, based on the 15 samples collected there in 1981. These two fields again appear to be relatively similar, but the difference of the weighted and unweighted fields, plotted in Figure 11, has a markedly higher amplitude than was apparent at the Bridgman, Michigan, site. Here the analyses suggest a more well-defined corridor of higher concentrations from the south, supportive of the hypothesis that the toxaphene was being transported from regions of application in the southern United States.

The unweighted probability field for Greenville, Mississippi, is plotted in Figure 12. The distribution of wind flow to the site on the days of sampling is more isotropic here than at either Bridgman or St. Louis, as indicated by the relative symmetry of the probability field about the receptor. The weighted probability field, shown in Figure 13, does not appear to be dissimilar to the unweighted field, but its difference from Figure 12, plotted as Figure 14, indicates that a relatively large bias is exhibited by the data. The corridor for higher concentrations of toxaphene at the Greenville site is associated with winds originating along the Gulf Coast. Winds from the north are systematically associated with lower than average concentrations.

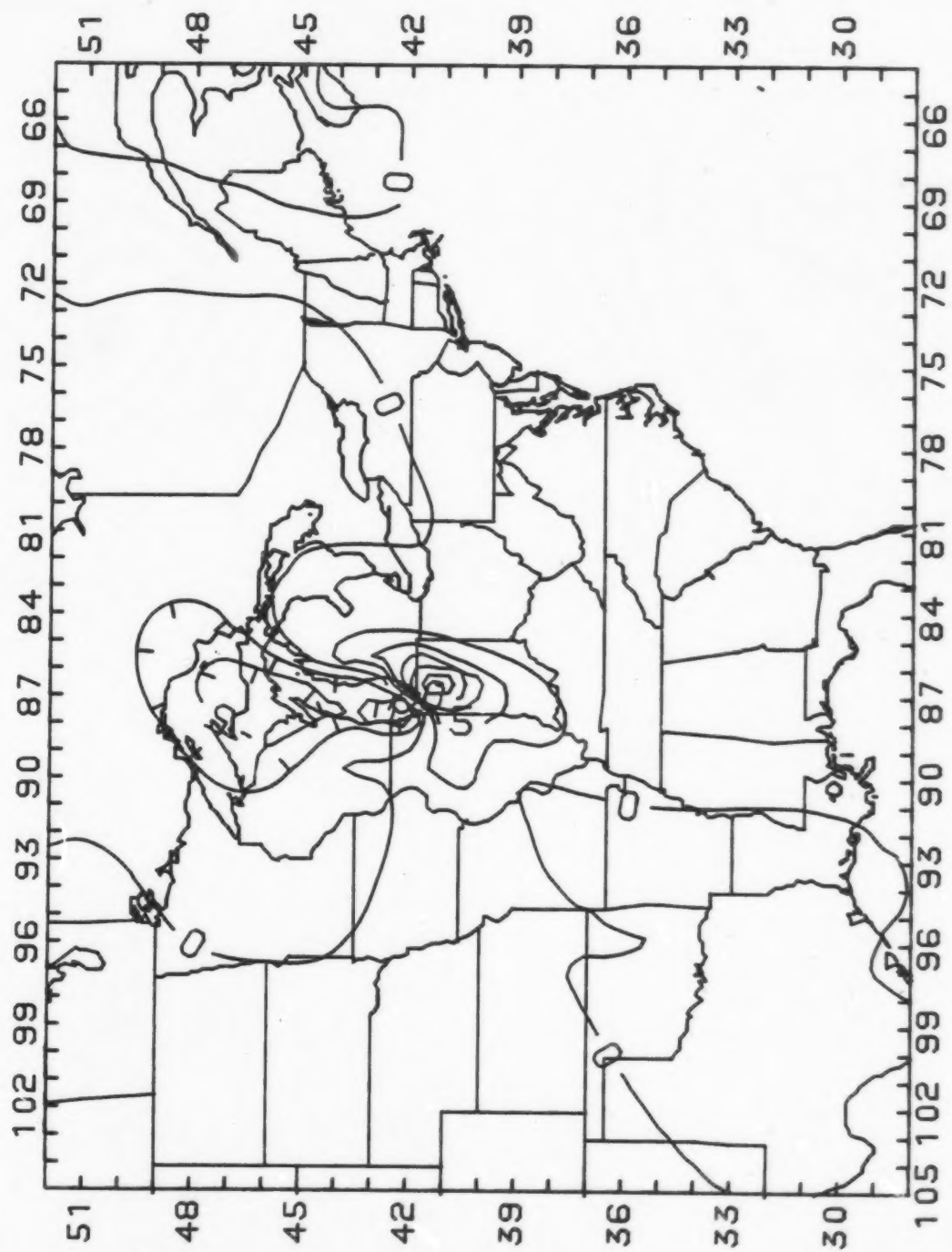


Figure 8. Difference between Figures 6 and 7.

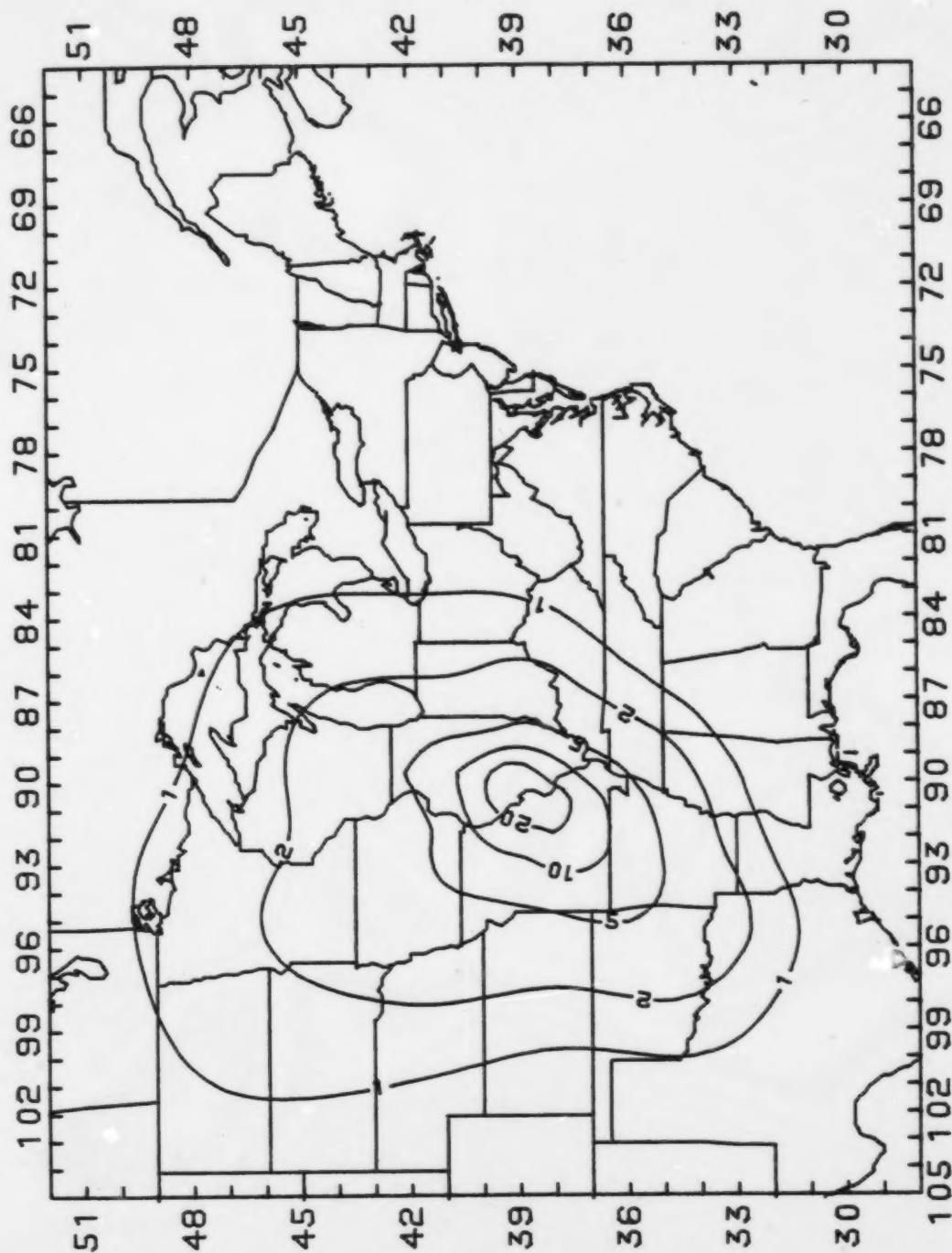


Figure 9. Unweighted probability of contribution during the sampling periods in units of $10^{-8}/\text{km}^2$ in St. Louis, Mo. (approximate center of concentric rings).

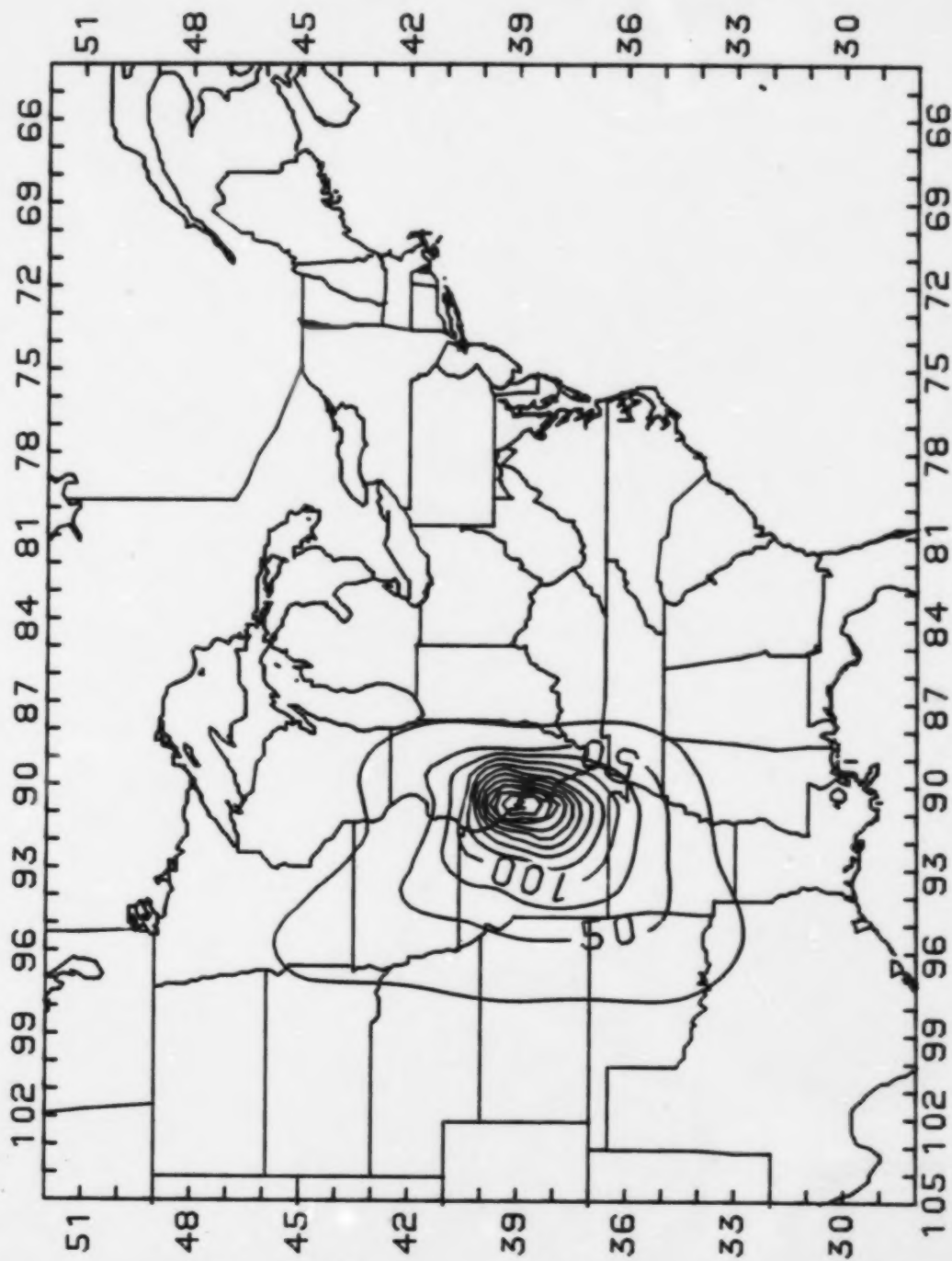


Figure 10. Weighted probability of contribution during the sampling periods in units of $10^{-8}/\text{km}^2$ in St. Louis, Mo.

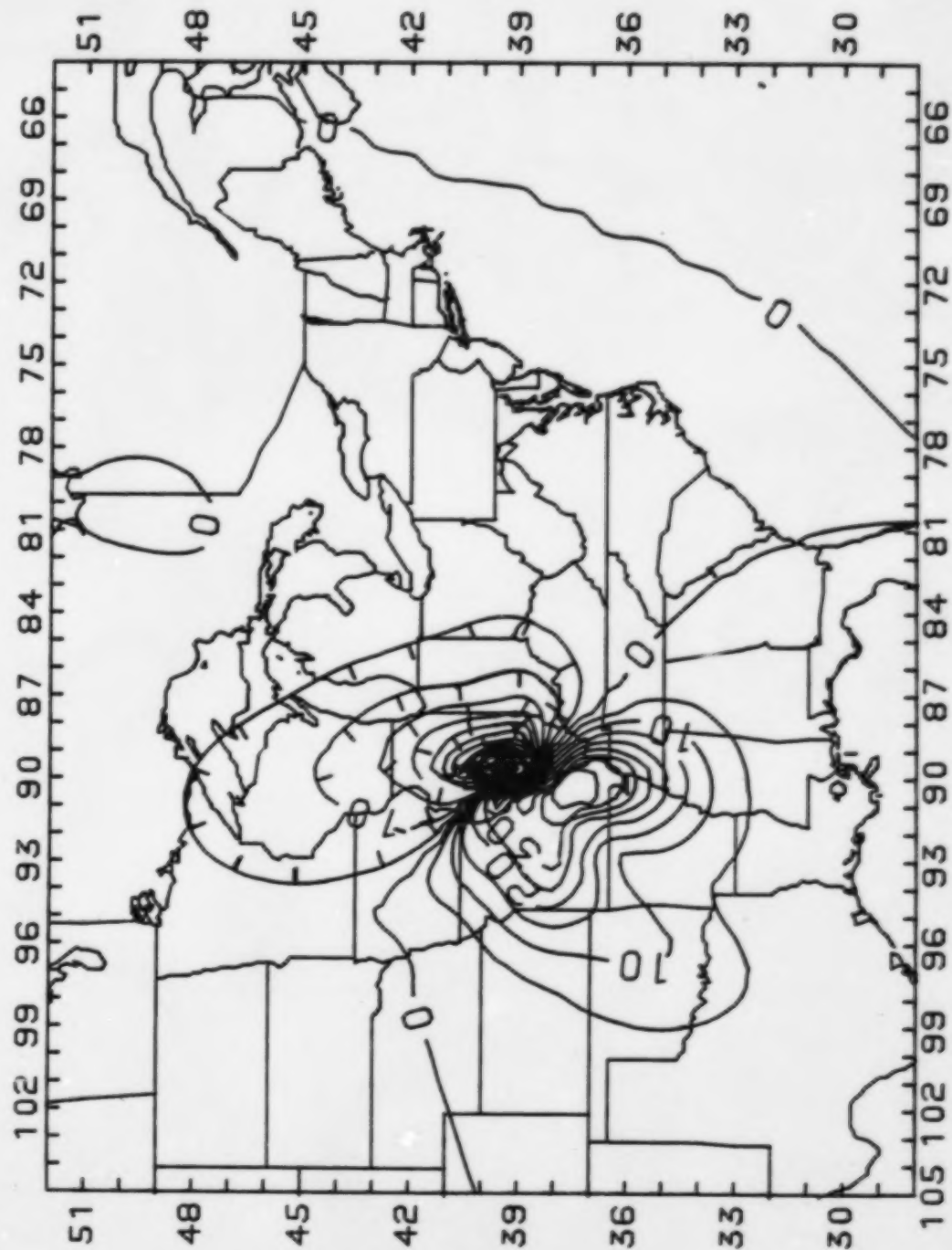


Figure 11. Difference between Figures 9 and 10.

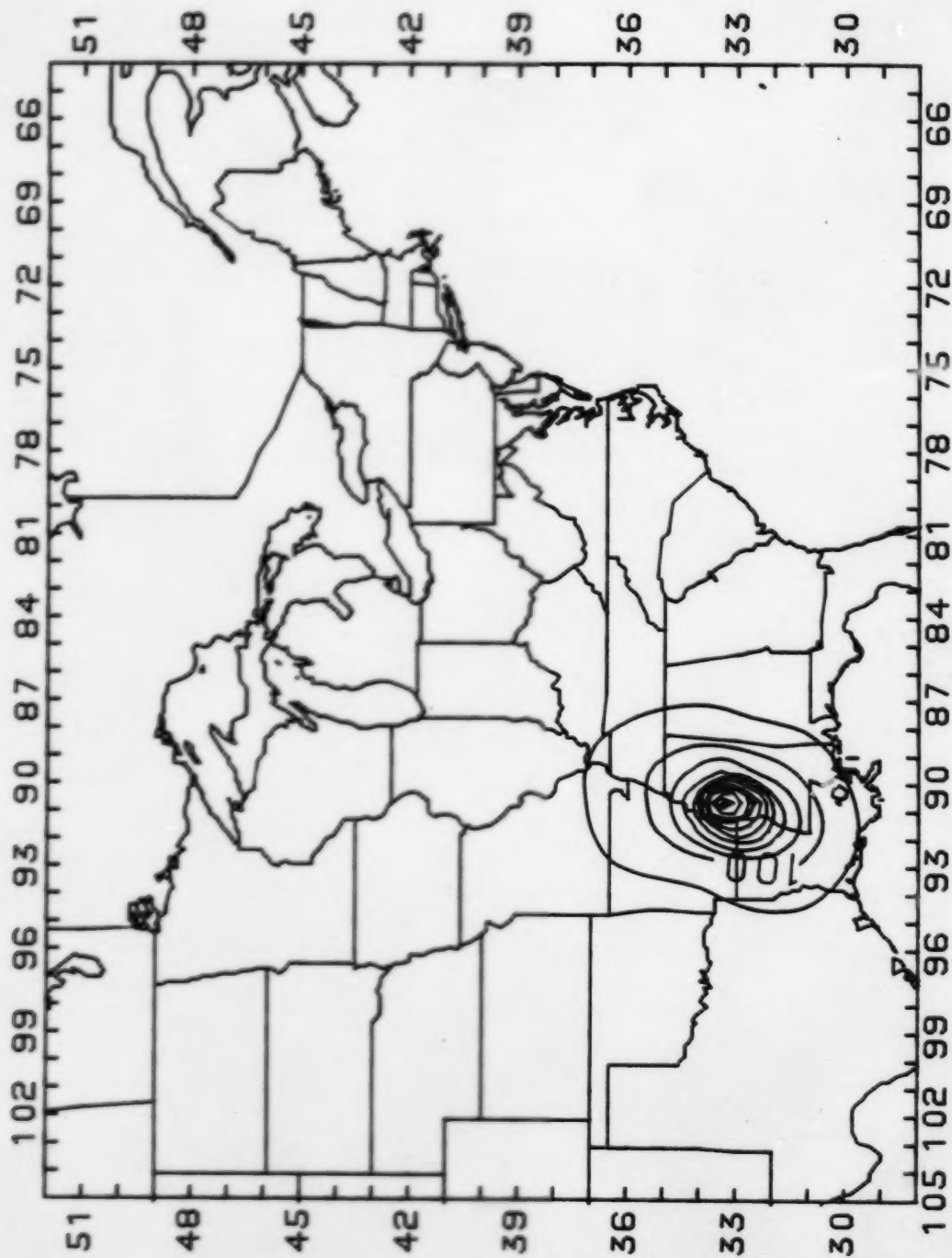


Figure 12. Unweighted probability of contribution during the sampling periods in units of $10^{-8}/\text{km}^2$ in Greenville, Miss. (approximate center of concentric rings).

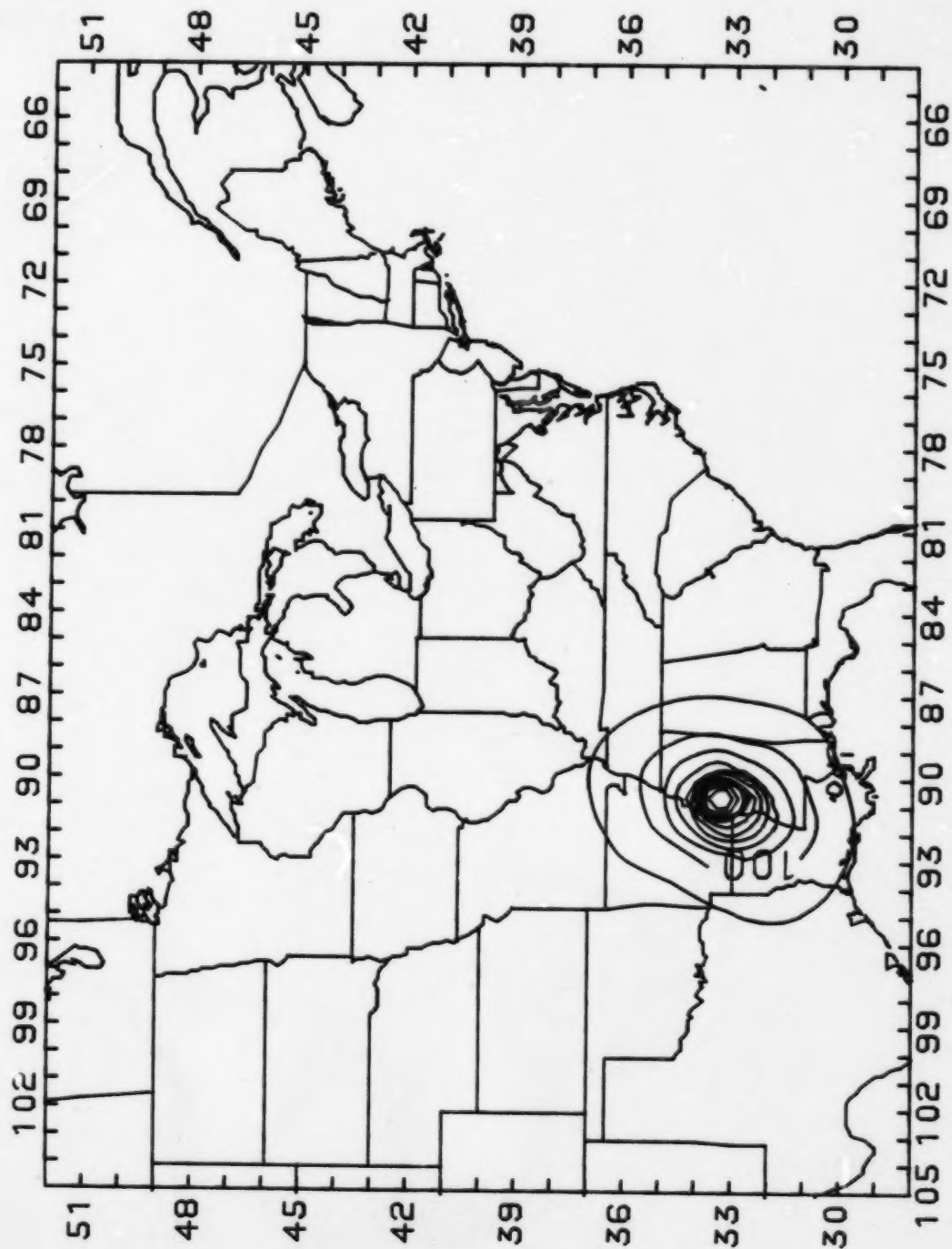


Figure 13. Weighted probability of contribution during the sampling periods in units of $10^{-8}/\text{km}^2$ in Greenville, Miss.

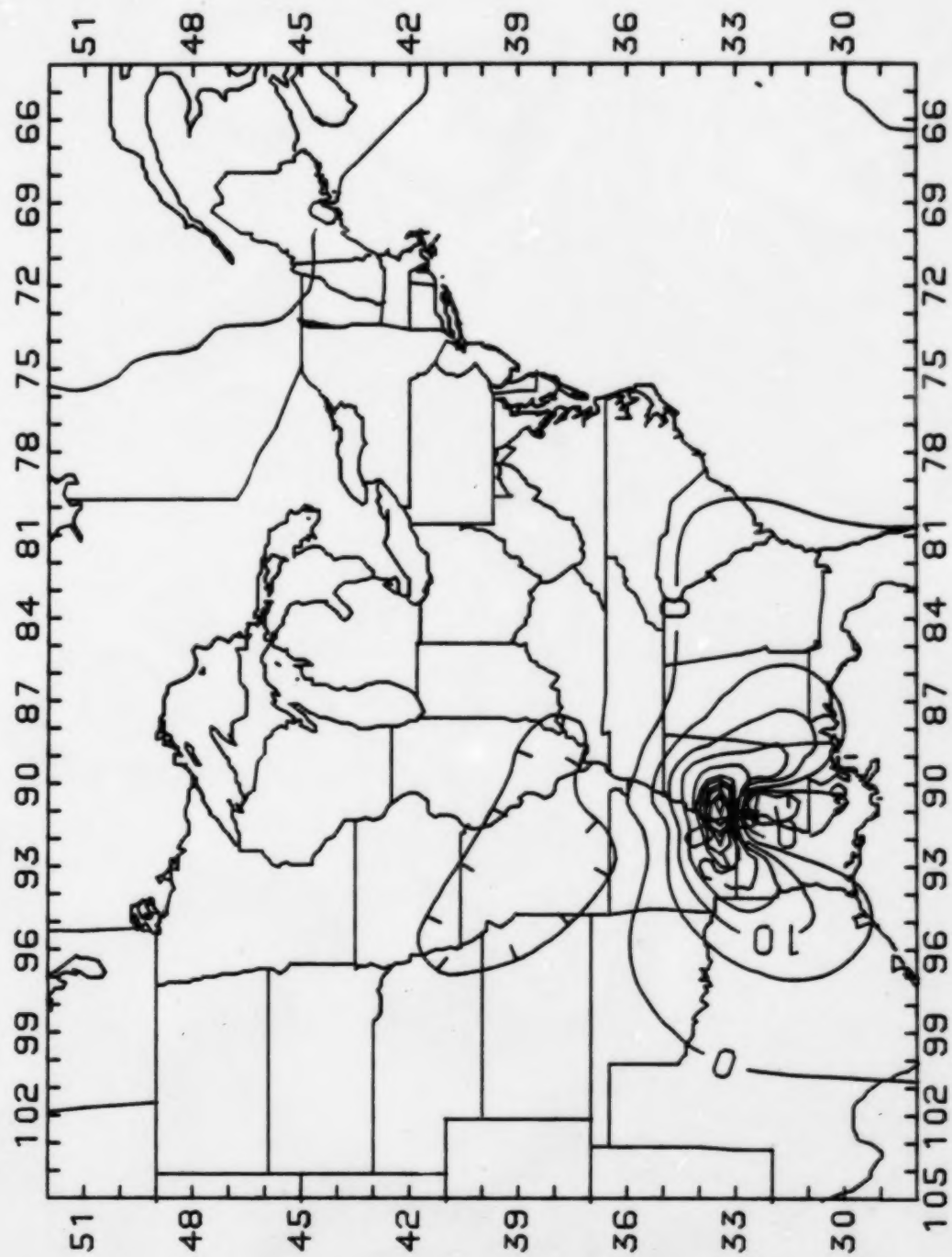


Figure 14. Difference between Figures 12 and 13.

The analysis of transport corridors for Beaver Island, Michigan samples was not conducted because only four samples were available for that site.

It has been assumed that each trajectory during the sample period was equally responsible for the observed concentration. However, without better temporal resolution in the sampling, it is difficult to assess the uncertainty inherent in this assumption. For comparison, the transport of atmospheric trace elements is highly episodic. The dry deposition of trace elements, assuming the process is proportional to the ambient concentration, is highest during specific episodes of roughly 3 or 4 days duration (cf. Husain and Samson 1980). The significance of such episodic contribution could be lost in this analysis if the episode were split by two or more long-period samples. The diagnostic methodology developed for this study is designed to be employed with a larger data base. The sample size available in this study limits the use of ensemble analyses.

Nonetheless, the results of this diagnostic analysis of the measured toxaphene concentrations shows a consistent pattern. At all measurement locations the toxaphene corridor was associated with southerly winds. The preferred corridors of transport of higher concentrations increased from northern to southern measurement sites, presumably in response to the larger range of concentrations in the south. This analysis is not capable of proving which source region(s) contributed to the observed concentrations, in part because so little is known about the magnitude of the source strengths. However, the methodology developed for this analysis is capable of identifying the probable corridors of transport which deliver the material to the receptor. The method is well suited for analysis of data which, because of low concentrations in the atmosphere, must be collected over long time periods

(greater than a day). With a sufficient number of samples, intra-period fluctuations in contribution to the sample will be removed and meaningful transport characteristics will be discerned.

ESTIMATES OF ATMOSPHERIC FLUX OF TOXAPHENE TO LAKE MICHIGAN

For this estimate the concentration over Lake Michigan was used as the immediate source for input. Our data provide a good estimate of this amount for August through November of 1981. Using the formulations proposed by Eisenreich et al. (1981) for estimating atmospheric flux of trace organics to the Great Lakes, total atmospheric loading to Lake Michigan for 1981 was estimated. For wet and dry flux, the general equations presented by Eisenreich et al. (1981) were:

$$F_w = C_r/s \cdot J \cdot SA \quad (1)$$

$$F_d = C_v/p \cdot V_d \cdot SA \quad (2)$$

F_w and F_d are wet and dry deposition, respectively; C_r/s = concentration in rain and snow; C_v/p = concentration in vapor and particulate; J = annual precipitation; V_d = deposition velocity; SA = lake surface area.

Wet Flux Calculation

For C_r/s the summer and winter concentration were estimated. Also a northern Lake Michigan (represented by Beaver Island), and a southern Lake Michigan level (represented by Bridgman) were computed. To do this calculation an average year-round air concentration was first estimated which could represent the whole lake. For the summer and fall of 1981, the average toxaphene in Bridgman was 0.35 ng/m^3 and for Beaver Island it was less than

1/2 of this amount. Therefore, as a whole lake estimate, these two concentrations were averaged, i.e.,

$$\frac{[0.35 \text{ ng/m}^3 + 0.35/2 \text{ ng/m}^3]}{2} = 0.26 \text{ ng/m}^3.$$

No direct observations were available for estimating a winter concentration (December to May) and no observation of input as snow has ever been reported. Therefore, to approximate what the air levels might have been, comparisons of summer to winter levels of toxaphene determined for air in South Carolina (Harder et al. 1980), and Bermuda (C. P. Rice, unpublished data) were available. These data indicated that approximately 2 to 4-fold decreases in atmospheric levels in winter could occur. Because of wind transport into Lake Michigan during winter months, was expected to be dominated by northern cold fronts, the lower estimate (1/4) was selected. Therefore, the toxaphene concentration estimated for the 6 winter months (December to May 1980-81) preceding the data presented here was $0.26 \text{ ng/m}^3/4$ or 0.065 ng/m^3 . An average yearly concentration for Lake Michigan air, northern and southern plus winter and summer, was calculated as

$$\frac{0.26 + 0.065}{2} = 0.16 \text{ ng/m}^3$$

This air concentration was next used to derive an expected yearly rain concentration. For this, a washout ratio was needed. The washout ratio from our one rain sample came out to 1,355

$$WR = \frac{\text{ng toxaphene/kg rain}}{\text{ng toxaphene/kg air}} \quad (3)$$

$$WR = \frac{31 \text{ ng/kg rain (28 Sept-1 Oct)}}{0.027 \text{ ng/(m}^3 = 1.18 \text{ kg) Air (28 Sept-1 Oct)}}$$

$$WR = 1,355$$

This greatly exceeded Bidleman's (Bidleman and Christensen 1979) highest observed value for washout ratios calculated from rainfall input of toxaphene in South Carolina (i.e., <16 to 861), and therefore appeared to be too high. As a compromise we chose a range of 500 to 1,000 for the likely range of washout ratio to be used in our calculations. Carrying out the calculation, rain concentrations were estimated to range from 68 to 136 ng/kg, e.g.,

$$\begin{aligned} 500 \text{ to } 1,000 &= \frac{\text{conc rain}}{0.16 \text{ ng/(m}^3 = 1.18 \text{ kg)}} \\ &= 68 \text{ to } 136 \text{ ng toxaphene/kg rain} \end{aligned}$$

Using these values in Eisenreich's formulation (Equation 1), the following was calculated:

$$\begin{aligned} \text{Flux wet} &= C_r/s \cdot J \cdot SA \quad (68 \text{ ng/L}) \\ &= (10^3 \text{ kg/m}^3) (68 \times 10^{-12} \text{ kg tox/kg rain}) (0.74 \text{ m/yr}) (5.9 \times 10^{10} \text{ m}^2) \\ &= 2,969 \text{ kg tox/yr at a rain concentration of } 68 \text{ ng toxaphene/kg rain} \\ &= 5,938 \text{ kg tox/yr at a rain concentration of } 136 \text{ ng toxaphene/kg rain} \end{aligned}$$

Dry Flux Calculation

For this calculation, the deposition velocity of $\leq 0.12 - 0.24$ cm/sec was taken from literature values presented by Bidleman and Christensen (1979) and Harder et al. (1982). The calculation for a 0.12 cm/sec was as follows:

$$F_d = C_v/p \cdot V_d \cdot SA$$

$$F_d = (60^2 \cdot 24 \cdot 365 \text{ sec/yr}) (0.16 \times 10^{-12} \text{ kg/m}^3)$$

$$(0.12 \times 10^{-2} \text{ m/sec}) (5.9 \times 10^{10} \text{ m}^2)$$

$$= 357 \text{ kg toxaphene/yr @ } V_d = 0.12 \text{ cm/sec}$$

$$= 715 \text{ kg toxaphene/yr @ } V_d = 0.24 \text{ cm/sec}$$

Comparing the relative input from the two processes, wet deposition appears to predominate, i.e., 3,000 to 6,000 kg/yr wet, versus 350 to 720 kg/yr for dry deposition.

A total flux would be 3,360 to 6,720 kg/yr for toxaphene from all atmospheric sources. These are similar to the estimated total input for PCB of 4,700 kg/yr for Lake Michigan (Murphy et al. 1982). However, Murphy's estimates indicated the largest input for PCBs are dry deposition processes, while our results indicate that rainfall is the predominant vector for toxaphene input. The greater likelihood of rainfall deposition dominating for toxaphene over other organochlorines (PCB, DDT, and chlordane) was also observed by Harder et al. 1982. It should finally be pointed out that the above calculations are based on a very limited data set, especially for the rainfall and dryfall estimates. Thus, the flux values which are derived must be considered speculative at this time. However, recent analytical data on residue levels in biota of the lakes suggest that the current levels of toxaphene are indeed similar to those of the PCBs (Rice and Evans, in press).

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APPENDIX A

TESTS FOR SILICIC ACID FRACTIONATION OF TOXAPHENE

In order to reduce the possibility of incorrect identification of gas chromatographic peaks which could co-elute with toxaphene, methods were investigated which were designed to selectively remove these interferences. The most problematic interferences expected were PCBs. Silicic acid chromatography has been reported to effectively separate toxaphene from PCBs (Bidleman et al. 1978).

METHODS

The silicic acid method in its complete form as proposed by Bidleman et al. (1978) was first tested. The water content of the original method was modified to contain 2.8% water rather than 3.3%. Also, the elution pattern was changed slightly so that separation of PCBs from DDT and chlordane was optimized. The elution pattern was as follows:

<u>Solvent</u>	<u>Vol.</u>	<u>Fraction</u>	<u>Compounds Expected</u>
petroleum ether	1- 10 mL	1	HCB
	10- 40 mL	2	~10% toxaphene, PCBs, DDE
	40-120 mL	3	~30% toxaphene, chlordane, DDT
dichloromethane	20 mL	4	60% toxaphene, dieldrin, DDD

To maximize toxaphene recovery for this study, we recombined fractions 3 and 4. Using this procedure recovery of toxaphene from column spikes was poor (20%, see Table A1). We then further modified the collection sequence by

taking only 2 fractions, i.e. 0 to 40 mL for PCB, HCB, and DDE and then a 20 mL methylene chloride sweep to secure the bulk of the toxaphene along with DDT, DDD, dieldrin, and chlordanes (Table A1, samples 2 and 3). With the 2 fraction procedure, recovery was improved but only marginally acceptable, i.e. 76 and 98%.

TABLE A1. SILICIC ACID RECOVERY OF TOXAPHENE

Method Used	# of Peaks Matched	Total Area Units		Percentage Recovered
		Spike Standard	Recovered Standard	
4-Fraction (F3 + F4 combined)	12/31	11.795	2.37	20.1
2-Fraction (20 mL DLM)	29/33	12.23	9.33	76.3
2-Fraction (20 mL DCM)	21/33	8.24	8.13	98.0

Based on these results, we decided that the fractionation procedures was not acceptable because recovery losses were too great. Such losses could not be risked, especially for the low level samples from Bridgman and Beaver Island. Furthermore, funds were not available to carry out these labor intensive procedures on the large number of samples generated during this study. Qualitatively, however, the method was a valuable confirmation tool. We applied the two fraction silicic acid method to one of the Bridgman air samples. In Figure A1, the unfractionated air sample can be compared to the first 40 mL eluate of the fractionated sample (the PCB fraction). An Aroclor

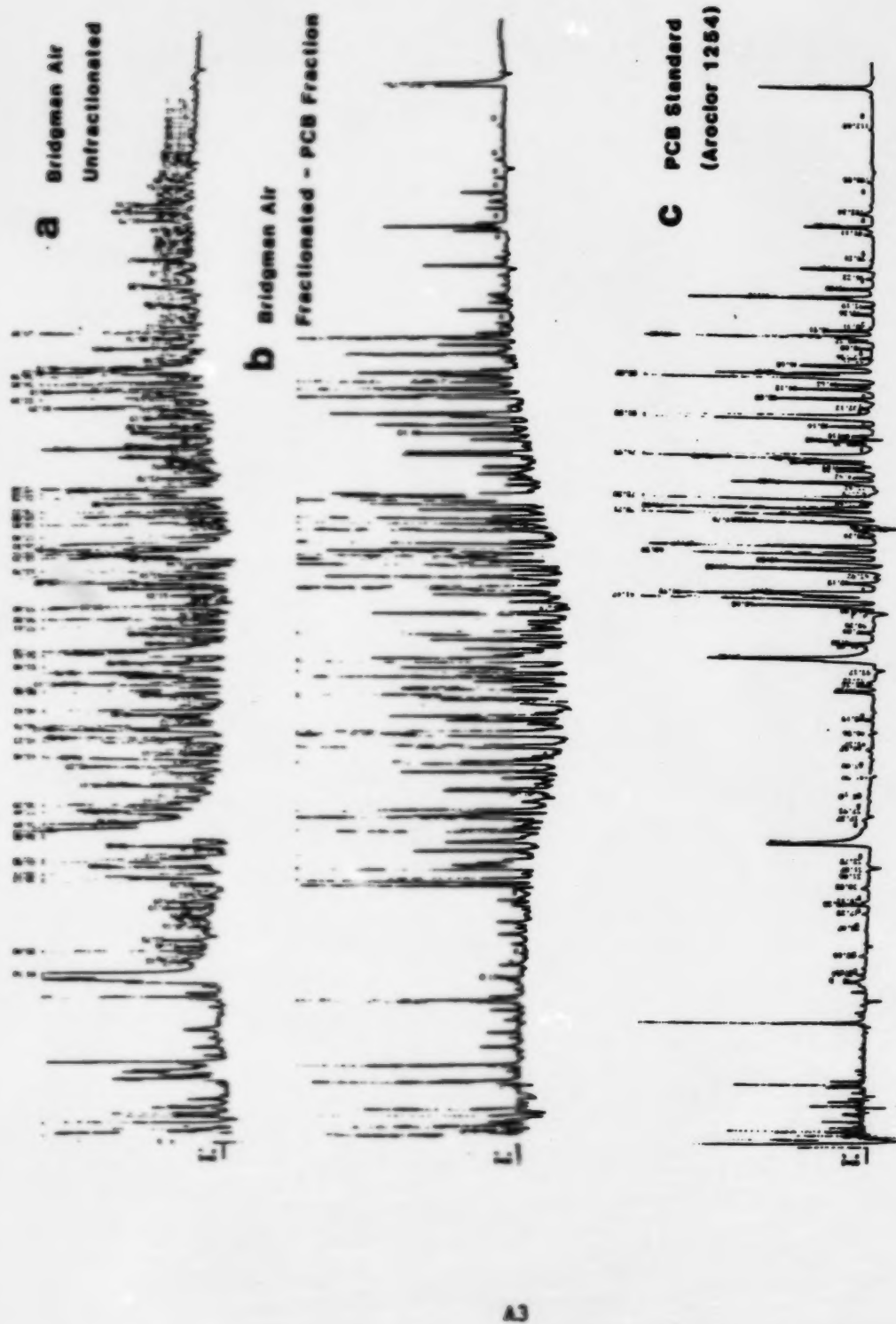


Figure A1. Capillary chromatograms of a) an unfractionated air sample from Bridgman, MI. (9 October to 11 October 1981) containing 0.66 ng/m³ toxaphene; b) PCB-containing fraction of the same air sample following silicic acid fractionation; and c) PCB standard (Aroclor 1254, 4 μ L 91.2 ng/mL).

1254 standard is also included in this figure as a representative PCBs for comparison with the fractionated sample. In Figure A2, the second fraction (toxaphene fraction) is shown along with the unfractionated air sample and a fractionated toxaphene standard.

It is clear that most of the peaks appearing in the unfractionated sample were eluted in the first fraction and many of them matched the PCB standard. This obviously reduced the potential for interference occurring in the second fraction (i.e., toxaphene fraction). Furthermore, the chromatograms of the fractionated toxaphene standard and the toxaphene fraction of the air sample can be compared visually and they do bear some similarities. (It is reassuring to get a visual impression that the matches are real and not just blindly trusting the data system to do peak matching.) Figure A3 has been included to indicate the relative distribution of peaks used for peak matching.

The toxaphene concentration calculated for the Bridgman air sample using unfractionated material, which was the general procedure adopted throughout this study, was 0.665 ng/m^3 . The concentration calculated using the fractionated sample and fractionated standard was 0.582 ng/m^3 . Therefore, the two methods showed good agreement. Furthermore, the peak matching for the unfractionated sample was 14 of 41 possible (34.1%), and for the fractionated sample it was 12 of 31 (39%). Therefore, removing the interferences did improve the matching as it should have. Another advantage of the fractionated method is that since PCBs are removed by the fractionation procedure, the peak selection criteria used for standards could have been altered so as to include peaks previously excluded from the peak table due to interferences with PCBs. This would have further expanded the peak table used for peak matching and most likely further improved the basis for toxaphene quantitation.

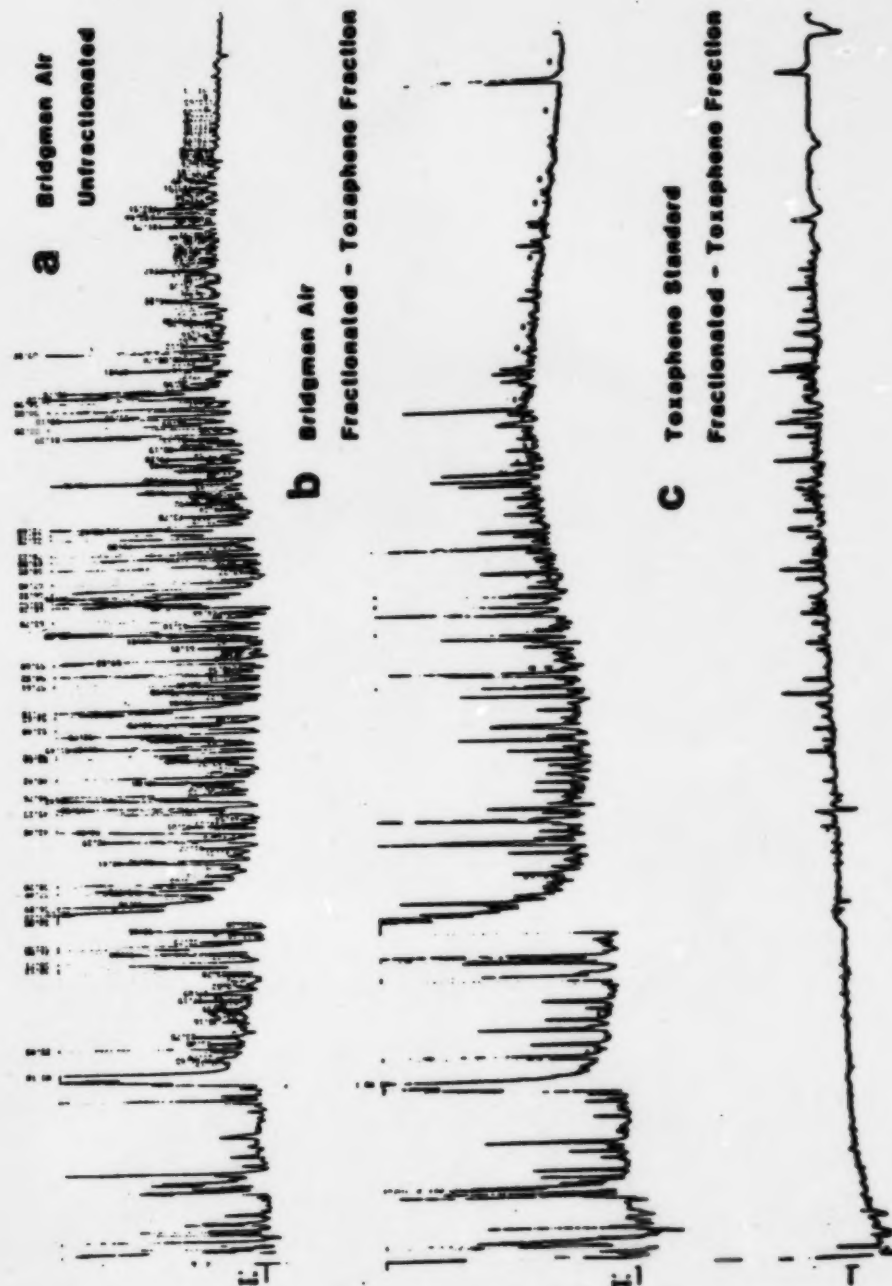


Figure A2. Capillary chromatogram of a) an unfractionated air sample from Bridgman, Mt. (9 October to 11 October 1981) containing 0.66 ng/m³ toxaphene; b) toxaphene-containing fraction of the same air sample following silicic acid fractionation; and c) toxaphene-containing fraction of a toxaphene standard following silicic acid fractionation.

TOXAPHENE STANDARD



- t - peaks selected to be matched with samples
- ocn - octachloronaphthalene, used as a reference peak

Figure A3. A representative chromatogram of an unfractionated toxaphene standard (444 ng/ μ L - 4 μ L injected).

APPENDIX B

LETTER TO HOUSTON WELLS, WELLS LABORATORIES, DESCRIBING
STUDY OF TOXAPHENE FORMULATIONS
USED IN GREENVILLE, MISSISSIPPI

C. Rice

Mr. R. Houston Wells
Wells Laboratories
RT 2 Box 714
Wilmont Rd.
Greenville, MS 38701

Dear Mr. Wells:

Enclosed you will find tabulated the results of our analytical comparison between four sources of toxaphene and two air samples taken in the Greenville area:

Toxaphene sources: *DFC 90-100*

- U.S. EPA Toxaphene Reference Standard
- Hercules 15FC 90-100
- Central America 90-100
- Drexel 616 form chem.

Samples:

- 3011-2 collected 9/1/81 to 9/29/81 Greenville, MS (185 m³ of air)
- 3018-2 collected 11/2/81 to 11/5/81 Greenville, MS (32 m³ of air)

Our comparisons were based on total peak matches (table 1), distribution of the matched peaks throughout the chromatogram (table 2) and the relative abundance, in terms of Area percent, for peaks within prescribed intervals throughout the chromatogram (table 3). Seventy-six peaks were chosen to represent toxaphene for our comparisons based on their relative abundance and non-interference with PCBs and other pesticides. Peak tables were constructed for each of the toxaphene sources using our previously analyzed EPA toxaphene standard. The analysis was performed on a Varian 3700 Gas-liquid chromatograph equipped with a Hewlett Packard 50 m., fused silica, SE-54 capillary column and electron capture detection. Runs were temperature programmed from 100°C to 245°C at 1°C per minute. Injector and detector temperatures were 270°C and 320°C respectively.

The primary purpose of this comparison was to select a toxaphene standard that best matched our samples. For both total matches (table 1) and distribution of those matches (table 2), the U.S. EPA toxaphene standard (tox. std.) showed the greatest consistency between samples. Greater than 50% of the peaks were matched, for both samples, at a tolerance of 0.004 e.g. relative retention time ± 0.004 . Those peaks that were matched appeared to be evenly distributed throughout the chromatogram as well. However, in terms of composition, greater than 50% of the total peak area was represented within the first two intervals (peaks 1 through 20, table 3) within which only about 25% of the matched peaks occurred.

We were also interested in similarities between the four toxaphene sources. Surprisingly, the peak matches between sources were relatively poor. Best matches occurred between tox. std. and Central America (53 matched peaks) and between Hercules and Drexel (58 and 64 matched peaks), (table 1). Differences between sources were also evident in the relative amount of material occurring

within the various peak intervals (table 3). Common to all sources however, was the relatively sparse abundance of material in the last two peak intervals.

Based on the aforementioned results, we feel that the U.S. EPA Reference Standard is best suited for analyzing samples collected in the Greenville area. We plan on continuing its use as our laboratory standard for future analysis.

Sincerely,

Clifford P. Rice
Clifford P. Rice

P.S. Notice that for sample 3018-2 in table 2 the highest peak match was for the Central American standard (perhaps this indicates a wind pattern link to a user of this specific brand during this sampling.) This was a short sampling interval and could be more source specific than sample 3011 which was a 28 day integrated sample. Table 3 does show a similarity between Hercules and the Toxaphene standard at least in relative percentage of peak areas represented by each 10 peak interval. The Drexel does appear to lack area for the later peaks in this comparison (this may be construed as Drexel having less persistence potential since these later peaks have heavier molecular weights and will be less volatile). Notice that from our air samples the heavier peaks were also lacking, thus confirming that the more volatile early GC eluters are enriched in the air as they should be due to their greater volatility. The Central American standard appears to be a good retention time match to our Toxaphene reference standard e.g. table 1 with 53 for toxaphene compared with Central America and 53 with Central America compared to toxaphene. Also, it appears to have a similar percentage area distribution over the 8-10 peak area intervals as was observed for the toxaphene and Hercules standards.

Table 1. Number of Peak matches between standards and two Greenville samples (3011-2 and 3018-2) at two tolerance levels. Total number of peaks chosen for comparison = 76.

<u>Standards Used for Comparison</u>				
<u>Tolerance = 0.004</u>	<u>Tox. Std.</u>	<u>Hercules</u>	<u>Central America</u>	<u>Drexel</u>
Tox. Std.	(76)*	35	53	45
Hercules	34	(76)*	31	64
Central America	53	35	(76)*	37
Drexel	41	58	32	(76)*
3011-2	40	33	25	32
3018-2	40	21	43	26
<u>Tolerance = 0.002</u>				
Tox. Std.	(76)*	11	27	19
Hercules	10	(76)*	15	50
Central America	31	17	(76)*	15
Drexel	19	47	12	(76)*
3011-2	26	13	10	24
3018-2	23	11	30	10

* Each peak table was adjusted to match 76 peaks when compared against itself.

Table 2. Numbers of peaks matched between two Greenville samples and four standards, peak intervals of 10 peaks per interval. Tolerance = 0.004.

<u>Numbers of Peak Matches Within the Specified Peak Range.</u>										
<u>Sample</u>	<u>Standard</u>	<u>Total</u>	<u>1-10</u>	<u>11-20</u>	<u>21-30</u>	<u>31-40</u>	<u>41-50</u>	<u>51-60</u>	<u>61-70</u>	<u>71-76</u>
3011-2	Tox. Std.	41	5	5	7	7	4	3	6	3
	Hercules	33	3	4	3	3	8	5	5	2
	Central									
	America	25	4	3	8	4	0	2	3	1
	Drexel	32	0	4	6	5	5	5	5	2
	Total									
3018-2	Tox. Std.	40	7	5	7	5	5	4	5	2
	Hercules	21	7	6	2	2	0	1	1	2
	Central									
	America	43	6	3	6	7	9	5	7	0
	Drexel	27	3	5	4	6	5	1	1	1
	Total									

Table 3. Percentage of Total Peak area within Peak intervals. Tolerance = 0.004.

Tox. Std.	<u>1-10</u>	<u>11-20</u>	<u>21-30</u>	<u>31-40</u>	<u>41-50</u>	<u>51-60</u>	<u>61-70</u>	<u>71-76</u>
Hercules	12.55	13.27	15.39	11.74	15.88	18.78	10.16	2.22
Central America	16.22	7.47	12.22	15.39	18.02	15.85	13.16	1.67
Drexel	19.70	14.04	19.29	11.75	14.88	11.50	5.49	3.34
*3011-2	19.20	43.38	9.20	15.93	3.62	5.04	3.22	0.42
*3018-2	12.47	38.61	12.04	11.96	13.91	7.10	3.63	0.28

*Greenville samples - Identified using EPA Toxaphene Reference Standard

Table 4. Average Retention times and Relative Retention times (RRT x 10) for peaks used on upper and lower limits of peak intervals referred to in tables 2 and 3. Reference peak was DDE (RT 70.70 min.)

Peak Number	Retention Time (min)	Relative Retention Time (RRT x 10)
1	44.53	6.30
10	56.36	7.972
11	57.24	8.100
20	67.99	9.617
21	68.36	9.670
30	74.30	10.509
31	70.44	10.533
40	77.86	11.014
41	78.46	11.098
50	85.56	12.103
51	85.93	12.154
60	90.94	12.864
61	91.06	12.884
70	98.67	13.958
71	99.51	14.076
76	100.37	15.048